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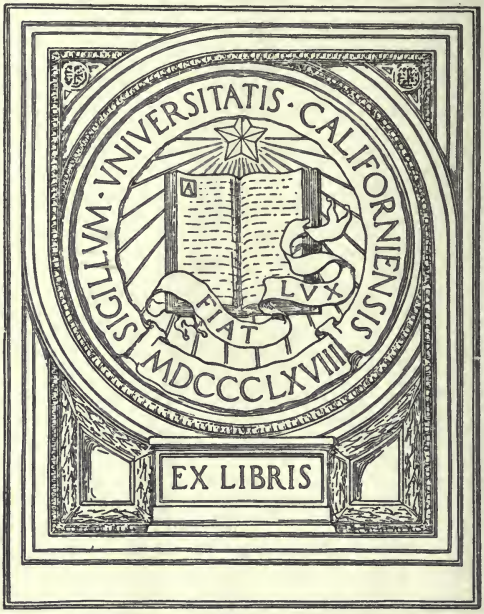

College of Pharmacy

ESSENTIALS

OF

VOLUMETRIC ANALYSIS

AN INTRODUCTION TO THE SUBJECT, ADAPTED TO THE NEEDS OF STUDENTS OF PHARMACEUTICAL CHEMISTRY

EMBRACING THE SUBJECTS OF ALKALIMETRY, ACIDIMETRY, PRECIPITATION ANALYSIS, OXIDIMETRY, INDIRECT OXIDATION, IODOMETRY, ASSAY PROCESSES FOR DRUGS, ESTIMATION OF ALKALOIDS, PHENOL, SUGARS, THEORY, APPLICATION AND DESCRIPTION OF INDICATORS

BY

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Illustrated

THIRD EDITION—REWRITTEN AND ENLARGED

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PREFACE TO THE THIRD EDITION

THE exhaustion of the second edition and the appearance of the new United States Pharmacopœia as well as the increasing demand for the book have necessitated a complete revision of "Essentials of Volumetric Analysis," and its issuance as a third edition.

The book has been considerably improved by the introduction of many new assay processes, among which may be mentioned the assays of mercuric salts, phosphates and hypophosphites by means of standard sulphocyanate solution; assays of chlorates, perborates, chloral, acetone, resorcinol, phenylsulphonates, arsenates, and alkali cacodylate.

The "c.c." has been replaced by "mil" and in other respects changes are made to accord with the new Pharmacopœia.

HENRY W. SCHIMPF.

NEW YORK CITY,
October, 1917.

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PREFACE TO THE FIRST EDITION

The growing need for a short text-book which will make the principles of volumetric analysis readily available without going too deeply into detailed and discursive description has led to the preparation of this elementary treatise.

In the following pages the aim is to present the principles of this interesting and important subject in a form readily intelligible to students and available for lecture-room and laboratory work. The essential points are condensed within the limits of a small book with the intention of furnishing an outline which may serve as a practical guide as well as an introduction to the more advanced and voluminous works on the subject.

If presented in a suitable manner volumetric analysis rarely fails to prove interesting to the student, because it gives him a clear conception of the quantitative significance of chemical equations and thus affords practical proofs of chemical laws; it furthermore trains the student to make careful observations, to form habits of accuracy in manipulation, and since the processes are easily carried out, enables him to arrive readily at a definite numerical conclusion.

The subject-matter in this book is systematically arranged as far as can be, and treated as concisely as is consistent with clearness of expression. The processes are grouped under five headings: Neutralization, Precipitation, Oxidation, Indirect Oxidation, and Iodometry. The principles underlying each

group are definitely indicated, and their application illustrated by numerous practical examples. Other subjects treated include methods of calibration and of the accurate reading of graduated instruments, the calculation of the results of analyses, the preparation and standardization of volumetric solutions. The indicators, their selection for special cases and the ionic theory regarding their action, as well as assay process for phenol, sugars and vegetable drugs also receive special treatment. The author hopes that he has prepared a book which will prove serviceable to those for whom it was written and that it will be as generously received as were the four editions of his Text-book of Volumetric Analysis.

HENRY W. SCHIMPF.

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Name.		Atomic Weight* based on O = 16.	Atomic Weight based on H = 1.	Approximate Atomic Weight.
Aluminium	Al.	27.1	26.9	27.0
Antimony	Sb.	120.2	119.3	120.0
Arsenic	As.	74.96	74.3	75.0
Barium	Ba.	137.37	136.4	136.0
Bismuth	Bi.	208.0	206.4	206.0
Boron	B.	11.0	10.9	11.0
Bromin	Br.	79.92	79.36	80.0
Cadmium	Cd.	112.40	111.6	111.0
Calcium	Ca.	40.07	39.8	40.0
Carbon	C.	12.005	11.91	12.0
Chlorin	Cl.	35.46	35.18	35.5
Chromium	Cr.	52.0	51.7	52.0
Cobalt	Co.	58.97	58.56	58.0
Copper	Cu.	63.57	63.1	63.0
Fluorin	F.	19.0	18.9	19.0
Gold	Au.	197.2	195.7	196.0
Hydrogen	H.	1.008	1.000	1.0
Iodin	I.	126.92	125.9	126.0
Iron	Fe.	55.84	55.5	56.0
Lead	Pb.	207.20	205.35	206
Lithium	Li.	6.94	6.98	7.0
Magnesium	Mg.	24.32	24.18	24.0
Manganese	Mn.	54.93	54.6	55.0
Mercury	Hg.	200.6	198.5	200.0
Molybdenum	Mo.	96.0	95.3	95.0
Nickel	Ni.	58.68	58.3	58.0
Nitrogen	N.	14.01	13.93	14.0
Oxygen	O.	16.00	15.88	16.0
Phosphorus	P.	31.04	30.77	31.0
Platinum	Pt.	195.2	193.3	194.0
Potassium	K.	39.1	38.86	39.0
Silver	Ag.	107.88	107.12	107.0
Sodium	Na.	23.00	22.88	23.0
Strontium	Sr.	87.63	86.94	87.0
Sulphur	S.	32.06	31.83	32.0
Tin	Sn.	118.7	118.1	118.0
Zinc	Zn.	65.37	64.9	65.0

* International Atomic Weights, 1916.

TABLE OF MULTIPLES OF SOME ATOMIC WEIGHTS AND COMBINATIONS IN FREQUENT USE.

	1	2	3	4	5	6	7	8	9
H	1.008	2.016	3.024	4.032	5.040	6.048	7.056	8.064	9.072
O	16.000	32.	48.	64.	80.	96.	112.	128.	144.
OH	17.008	34.016	51.024	68.032	85.04	102.048	119.056	136.064	153.072
H_2O	18.016	36.032	54.048	72.064	90.08	108.096	126.112	144.128	162.144
N	14.01	28.02	42.03	56.04	70.05	84.06	98.07	112.08	126.09
NH_3	17.034	34.064	51.102	68.128	85.170	102.204	119.238	136.272	153.306
NH_4	18.042	36.084	54.126	72.168	90.210	108.252	126.294	144.336	162.378
NO_2	46.01	92.02	138.03	184.04	230.05	276.06	312.07	388.08	414.09
NO_3	62.01	124.02	186.03	248.04	310.05	372.06	434.07	496.08	558.09
C	12.00	24.	36.	48.	60.	72.	84.	96.	108.
CO_2	44.00	88.	132.	176.	220.	264.	308.	352.	396.
CO_3	60.00	120.	180.	240.	300.	360.	420.	480.	540.
CN	26.01	52.02	78.03	104.04	130.05	156.06	182.07	208.08	234.09
Cl	35.46	70.92	106.38	141.84	177.3	212.76	248.22	283.68	319.14
Br	79.92	159.84	239.76	319.68	399.6	479.52	559.44	639.36	719.28
I	126.92	253.84	380.76	507.68	634.6	761.52	888.44	1015.36	1142.28
S	32.07	64.14	96.21	128.28	160.35	192.42	224.49	256.56	288.63
SO_3	80.07	160.14	240.21	320.28	400.35	480.42	560.49	640.56	720.63
SO_4	96.07	192.14	288.21	384.28	480.35	586.42	672.49	768.56	864.63
PO_4	95.04	190.08	285.12	380.16	475.20	580.24	665.28	760.32	855.36
P_2O_5	142.08	284.16	426.24	568.32	710.40	852.48	994.56	1136.64	1278.72
Na	23.00	46.	69.	92.	115.	138.	161.	184.	207.
K	39.10	78.20	117.30	156.40	195.50	234.60	273.70	312.80	351.90
Li	6.94	13.88	20.82	27.76	34.70	41.64	48.58	55.52	62.46
Ca	40.07	80.14	120.21	160.28	200.35	240.42	280.49	320.56	360.63
Ba	137.37	274.74	412.11	549.48	686.85	824.22	761.59	898.96	1036.33
Ag	107.88	215.76	323.64	431.52	539.40	647.28	755.16	863.04	970.92
Fe	55.84	111.68	167.52	223.36	279.20	335.04	390.88	446.72	502.56
Hg	200.6	401.2	601.8	802.4	1003.0	1203.6	1404.2	1604.8	1805.4

ABBREVIATIONS AND SIGNS

cc.....cubic centimeter

gm.....gramme, 15.43235 grains

gr.....grain

at. wt.....atomic weight

V.S.....volumetric solution

T.S.....test solution.

U. S. P.....United States Pharmacopœia.

$\frac{N}{1}$.....normal.

$\frac{N}{10}$.....decinormal.

$\frac{N}{100}$.....centinormal.

$\frac{N}{2}$.....semi-normal.

$\frac{2}{N}$ or 2N.....double-normal.

mil.....milliliter.

THE ESSENTIALS OF VOLUMETRIC ANALYSIS

CHAPTER I

INTRODUCTION

In a chemical analysis the aim is to determine the nature of the chemical substances contained in a given compound or to ascertain their quantities. In the former case the analysis is a *qualitative*, in the latter a *quantitive*, one.

The quantitive analysis of a substance may be made either by the *gravimetric* or the *volumetric* method.

The Gravimetric Method consists in separating and weighing the constituents either in their natural states or in the form of new and definite compounds, the composition of which is known to the analyst. From the weights of these new compounds the analyst can calculate the quantities of the original constituents.

Example. To determine the quantity of silver in a solution by the gravimetric method we proceed as follows:

Ten grams of a solution containing silver in the form of silver nitrate ($AgNO_3$) is placed into a beaker, and, after slightly acidulating with nitric acid, is treated with hydrochloric acid, drop by drop, until no further precipitation occurs. The precipitate which consists of silver chlorid (AgCl) is then separated by filtration, thoroughly washed, dried and weighed. Its weight is found to be 0.69 gm. The calculation is then made as follows: 143.34 gms. of silver chlorid

represents 107.88 gms. of silver or 169.89 gms. of silver nitrate, as the equation shows:

$$\underset{169.89}{AgNO_3} + HCl = \underset{143.34}{AgCl} + HNO_3.$$

Therefore, 0.69 gm. of silver chlorid will represent

$$\frac{107.88}{143.34} \times 0.69 = 0.519 \text{ gm. of silver,}$$

or

$$\frac{169.89}{143.34} \times 0.69 = 0.817 \text{ gm. of silver nitrate.}$$

The Volumetric Method. This method depends upon the use of solutions (*standard solutions*) which are of known strength and paying attention to the valume of such a solution which must be added to the substance under analysis to perform with it and complete a certain reaction. Thus, if we conduct an analysis by means of such a solution, and can express by a chemical equation the reaction which takes place, we can readily and accurately calculate the quantity present of the substance under analysis.

Example. If a silver solution is to be analyzed by this method it is treated with a standard solution of sodium chlorid, added slowly from a burrette until no more silver chlorid is precipitated. Each mil of this standard solution will precipitate a certain weight of silver as silver chlorid, and hence by noting the number of mils used to complete the precipitation, the weight of the silver in the solution analyzed is easily ascertained.

The $\frac{N}{10}$ sodium chlorid solution is generally used for this purpose. It is made by dissolving $\frac{1}{10}$ of the molecular weight of the salt (in grams) (5.846 gms.) in sufficient water to make 1000 mils. 1000 mils of this solution will precipitate $\frac{1}{10}$ of the atomic weight of silver (in grams) (10.788 gms.). and

hence each mil of the sodium chlorid solution represents 0.010788 gm. of metallic silver, and by multiplying this figure by the number of mils of the sodium chlorid solution used, the quantity of silver in the solution under analysis is ascertained. If in the above analysis 100 mils of the $\frac{N}{10}$ sodium chlorid solution were used, then $0.010788 \times 100 = 1.0788$ gms. of metallic silver.

The reaction is illustrated by this equation:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

10) 107.88 10) 58.46

1000) 10.788 gms. 1000) 5.846 gms. = 1000 mil $\frac{N}{10}$ V.S.

0.010788 gm. 0.005846 gm. = 1 mil " "

From the examples given it will be seen that the gravimetric operations consume no little time, and require the exercise of considerable skill. The washing of the precipitate must be thoroughly performed in order that it be freed from all adhering matter. The drying also is a matter of some consequence and must be performed in such a manner as to prevent the admixture of dust or the decomposition of the precipitate by excessive heat. A very accurate balance is also required.

The volumetric operations, on the other hand, do not require that the substance to be determined be separated in the form of a compound of known composition and weighed in the dry state; in fact, the substance may be accurately estimated when mixed with many others. It therefore obviates the necessity for the frequent separations and weighings which the gravimetric method demands, and enables the analyst to do the work in a very short time.

The instruments needed for volumetric work are few and simple, and comparatively little skill is required. Furthermore, the results obtained are in most instances more accurate.

CHAPTER II

GENERAL PRINCIPLES OF CHEMICAL COMBINATION UPON WHICH VOLUMETRIC ANALYSIS IS BASED

1. When substances unite chemically the union always takes place in definite and invariable proportions. Thus when silver nitrate and sodium chlorid are brought together, 169.89 parts (by weight) of silver nitrate and 58.46 parts (by weight) of sodium chlorid will react with each other, producing 143.34 parts of a curdy white precipitate (silver chlorid).

These substances will react with each other in these proportions only.

If a greater proportion of silver nitrate than that above stated be added to the sodium chlorid, only the above proportion will react, the excess remaining unchanged.

The same is true if sodium chlorid be added in excess of the above proportions. For instance, if 200 parts of silver nitrate be mixed with 58.46 parts of sodium chlorid, 169.89 parts only will react with the sodium chlorid, while 30.11 parts of silver nitrate will remain unchanged. Again, when potassium hydroxid and sulphuric acid are mixed potassium sulphate is formed, 112.2 parts of potassium hydroxid and 98.1 parts of sulphuric acid being required for complete neutralization. These two substances unite chemically in these proportions only.

The equation is

$$\underset{112.2}{2KOH} + \underset{98.1}{H_2SO_4} = K_2SO_4 + 2H_2O.$$

In other words, 112.2 parts of KOH will neutralize 98.1 parts of H_2SO_4, and consequently 98.1 parts of H_2SO_4 will neutralize 112.2 parts of KOH.

Oxalic acid and sodium carbonate react upon each other in the proportions shown in the equation

$$\underset{126.05}{H_2C_2O_4 \cdot 2H_2O} + \underset{106}{Na_2CO_3} = Na_2C_2O_4 + CO_2 + 3H_2O.$$

126.05 parts of crystallized oxalic acid are neutralized by 106 parts of anhydrous sodium carbonate.

2. Definite chemical compounds always contain the same elements in exactly the same proportions, the proportions being those of their atomic weights, or some multiple of these weights.

Thus sodium chlorid (NaCl) contains 23 parts of metallic sodium and 35.46 parts of chlorin, these being the atomic weights of sodium and chlorin respectively.

Potassium sulphate (K_2SO_4) contains twice $39.1 = 78.2$ parts of potassium, 32.07 parts of sulphur, and four times $16 = 64$ parts of oxygen.

Potassium hydroxid (KOH) contains 39.1 parts of potassium, 16 parts of oxygen, and one part of hydrogen. Hydrochloric acid (HCl) contains one part of hydrogen and 35.46 parts of chlorin.

Upon these facts the volumetric methods of analysis are based.

It has been shown that 98.1 gms. of sulphuric acid will neutralize 112.2 gms. of potassium hydroxid. It is therefore evident if a solution of sulphuric acid be made containing 49.05 gms. of the pure acid in 1000 mils, that one mil of this solution will neutralize 0.0561 gm. of potassium hydroxid. In estimating alkalies with this acid solution, the latter is

added from a burette, in small portions, until the alkali is neutralized, as shown by its reaction with some indicator.

Each mil of the acid solution required before neutralization is complete indicates 0.0561 gm. of KOH, and the number of mils used multiplied by 0.0561 gm. gives the quantity of pure KOH in the sample analyzed.

One mil of the same solution will neutralize 0.04 gm. of sodium hydroxid (NaOH), 0.053 gm. of anhydrous sodium carbonate (Na_2CO_3), etc.

If a solution of crystallized oxalic acid be made by dissolving 63.02 gms. in sufficient water to make 1000 mils, we will have a normal solution, the neutralizing power of which is exactly equivalent to the above mentioned normal sulphuric acid solution.

The strength of acids is estimated by alkali volumetric solutions. A normal solution of potassium hydroxid containing 56.1 gms. in the liter will neutralize exactly 1 liter of the normal acid solution; 1 mil of this normal alkali will neutralize 0.03646 gm. of HCl, 0.06362 gm. of $H_2C_2O_4$, or 0.04905 gm. of H_2SO_4, etc.

CHAPTER III

VOLUMETRIC OR STANDARD SOLUTIONS

ANY solution employed in volumetric analysis for the purpose of estimating the strength of substances, that is, any solution the chemical power or titer of which has been determined, is designated a *standard* or *volumetric solution.* Such a solution is said to be "titrated" (French *titre* = title or power), and is sometimes also called a *set* solution or a *standardized* solution. It may be normal, decinormal, empirical, or of any strength, so long as its strength is known.

When volumetric analysis first came into use the solutions were so made that each substance to be estimated had its own special volumetric solution, and this was usually of such strength as to give the result in percentages. Thus a certain strength of standard acid was employed for potash, another for soda, and a third for ammonia, and in testing the acids, each had its own special standard alkali. These solutions were known as normal solutions; they are still to some extent in use, and since solutions now designated as normal are of an entirely different character, it is important that no misconconception should exist when a normal solution is spoken of.

Normal Solutions are those which contain one liter (1000 mils), the molecular weight of the active reagent expressed in grams, and reduced to the valency corresponding to one atom of replaceable hydrogen or its equivalent. In other words, those which contain in 1000 mils in any given reaction the chemical equivalent of one gram of hydrogen. The now accepted basis for the atomic weights O = 16 makes a slight

change in the quantity of reagent in a normal solution, i.e., it will contain in 1000 mils the exact equivalent of 8 gms. of oxygen.

Thus in univalent or monobasic compounds the full molecular weight in grams is contained in a liter of the normal solution.

Example. Hydrochloric acid, HCl, having one replaceable hydrogen atom, its normal solution would contain the full molecular weight, 36.46 gms. in a liter. A normal solution of potassium hydroxid should contain 56.1 gms. of KOH in a liter, while that of sodium hydroxid should contain 40 gms. of absolute NaOH.

Normal solutions of bivalent or dibasic compounds contain in 1000 mils one-half the molecular weight in grams. Thus, oxalic acid, $H_2C_2O_4 + 2H_2O = 126.05$, having two replaceable H atoms, one-half of its molecular weight in grams $= 63.02$ is contained in a liter of its normal solution. For the same reason a liter of a normal solution of sulphuric acid contains $\frac{98.1}{2} = 49.05$ gms., and a liter of a normal solution of sodium carbonate Na_2CO_3 contains $\frac{106}{2} = 53$ gms., while in the case of trivalent or tribasic compounds one-third of the molecular weight in grams is contained in a liter of the normal solution.

Thus it will be seen that one mil of any normal acid solution will neutralize one mil of any normal alkali solution, because one molecule of a univalent acid will neutralize one molecule of a univalent alkali, or a half a molecule of a bivalent alkali. This is shown by the equations

$$\underset{36.46}{HCl} + \underset{46}{NaOH} = NaCl + H_2O,$$

$$\underset{2)72.92}{\underset{36.46}{2HCl}} + \underset{2)106}{\underset{53}{Na_2CO_3}} = 2NaCl + H_2O + CO_2.$$

The value of a reagent as expressed by its hydrogen equivalent is readily seen in the case of acids and alkalies by reference to the chemical formula, but in such standard solutions as potassium dichromate, potassium permanganate, sodium thiosulphate, and others, the particular reaction in any given analysis must be taken into account in making a normal solution; for instance, when $K_2Cr_2O_7$ is to be used as a precipitating agent, its reaction is as follows:

$$2Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2.$$

It is thus seen that one molecule of $K_2Cr_2O_7$ will cause the precipitation of two atoms of barium in the form of chromate. Each atom of barium is chemically equivalent to two atoms of hydrogen; therefore one-fourth of a molecule of $K_2Cr_2O_7$ is equivalent to one atom of hydrogen. And therefore a normal solution of this salt, when used as a precipitating agent, must contain in one liter one-fourth of its molecular weight in grams; $\frac{294.2}{4} = 73.55$ gms.

If $K_2Cr_2O_7$ is to be used as an oxidizing agent, the three atoms of oxygen which it yields for oxidizing purposes must be taken into account. When this salt oxidizes it splits up into $K_2O + Cr_2O_3 + O_3$. The three atoms of oxygen combine with and oxidize the salt acted upon, or they combine with an equivalent quantity of the hydrogen of an acid and liberate the acidulous part, which then combines with the salt. As the equations show,

$$6FeO + K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3Fe_2O_3 \quad \text{or} \quad (Fe_6O_9);$$

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 7H_2O + K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3;$$

$$7H_2SO_4 + K_2Cr_2O_7 = 3SO_4 + 7H_2O + K_2SO_4 + Cr_2(SO_4)_3.$$

Each of these atoms of oxygen are equivalent to two atoms of hydrogen. Thus O_3 is equivalent to H_6.

Hence a liter of a normal solution of $K_2Cr_2O_7$, when used as an oxidizing agent, contains one-sixth of its molecular weight in grams.

The same may be said of potassium permanganate when used as an oxidizing agent.

$2KMnO_4$ has five atoms of oxygen which are available for oxidizing purposes, and each of these is capable of taking two atoms of hydrogen from an acid and liberating the acidulous part. The hydrogen equivalent of this salt may therefore be said to be one-tenth of the weight of $2KMnO_4$, and a normal solution of this salt contains 31.606 gms. in a liter.

Sodium Thiosulphate (Hyposulphite), $Na_2S_2O_3$, is another instance. The molecule of this salt has two atoms of sodium, which have replaced two atoms of hydrogen of thiosulphuric acid. Thus it would seem that a normal solution should contain one-half of the molecular weight in grams. But the particular reaction of this salt with iodin is taken into account.

One molecule reacts with one atom of iodin, as seen in the equation

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Since iodin is univalent, a molecule of the salt is equivalent to one atom of hydrogen.

A normal solution of this salt therefore contains the molecular weight in grams in a liter.

Decinormal Solutions, $\frac{N}{10}$, are one-tenth the strength of normal solutions.

Centinormal Solutions, $\frac{N}{100}$, are one-hundredth the strength of normal solutions.

Seminormal Solutions, $\frac{N}{2}$, are one-half the strength of normal solutions.

Double-normal Solutions, $\frac{2}{N}$, are twice the strength of the normal.

Empirical Solutions. A solution which does not contain an exact atomic proportion of the reagent may be employed as a volumetric solution after its strength or titer has been determined. Such a solution is said to be *empirical*, and solutions of this sort are very frequently used. To prepare solutions of exactly normal strength is a tedious process and often inconvenient. If the solution is approximately normal and its strength accurately determined, it may be used as it is. Again, in the case of standard solutions of the caustic alkalies, which, when not kept with all precautions, deteriorate readily through absorption of carbon dioxid from the air, as well as through their action upon the glass containers. To restore the titer of such solutions by the introduction of more of the alkali is an unnecessary waste of time, inasmuch as it is only necessary to determine its exact strength and then use it as it is. For instance, if an approximately normal solution of potassium hydroxid is on hand, its strength is determined as follows:

Ten mils of an exactly normal oxalic or other acid solution are put into a beaker, and after diluting with a little water, and adding three or four drops of methyl orange, the empirical potassium hydroxid solution is run in from a burette until the color of the solution changes from red to yellow; the number of mils required is then noted.

Assuming that 10.4 mils were required to neutralize the 10 mils of normal acid, hence its strength is $\frac{100}{104}$ or 0.9615, that of a strictly normal solution, and the number of

mils used in any estimation must be multiplied by $\frac{100}{104}$ or 0.9615, and then by the normal factor for the substance analyzed.

It is a good plan to have the factor marked on the label of the bottle containing such an empirical solution. In this case it would be $\times 0.9615 = \text{normal}$.

Standard solutions for use in volumetric analysis are usually solutions of acids, bases, or salts, and in two cases elements, namely, iodin and bromin.

A standard solution of a base is usually used for the estimation of free acids.

A standard solution of an acid is usually used for the estimation of a free base, or the basic part of a salt, the acid of which can be completely expelled by the acid used in the standard solution. Example, carbonates.

A standard solution of a salt may be used as a precipitant, or it may be used as an oxidizing or reducing agent.

That part of the reagent in a standard solution which reacts with the substance under analysis is the active constituent of the solution. As Ag in $AgNO_3$ is the active constituent of the standard solution of silver nitrate,

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

or Cl in NaCl, is the active constituent of the standard solution of sodium chlorid.

If the reagent is a base, as KOH, the basic part K is the active constituent. If the reagent is an acid, the active constituent is the acidulous part, as SO_4 in H_2SO_4.

If the action of the reagent is oxidizing, then that part of the reagent which produces the oxidation is the active constituent.

The valence of an acid is shown by the number of replace-

able hydrogen atoms it contains. Thus HCl is univalent, H_2SO_4 is bivalent, which means that a molecule of HCl is chemically equivalent to one atom of hydrogen, and a molecule of H_2SO_4 is chemically equivalent to two atoms of hydrogen.

The valence of a base is shown by the number of hydroxyls it is combined with. As KOH is univalent, $Ca(OH)_2$ is bivalent.

The valence of a salt is shown by the equivalent of base which has replaced the hydrogen of the corresponding acid.

Thus NaCl, in which Na has replaced H of HCl, is univalent.

K_2SO_4, in which K_2 has replaced H_2 of H_2SO_4, is bivalent.

Preparation of Volumetric Solutions. In preparing volumetric solutions it must be borne in mind that most salts when dissolved in water cause a condensation in volume, through reduction of temperature, while some substances, as for instance sulphuric acid and alkali hydroxids, cause a rise in temperature and a consequent increase in volume. It is therefore necessary, after making a solution, to set it aside for a short time, in order to allow it to attain the proper temperature before measuring it.

It is always the best plan to take a weighed quantity of the salt, slightly greater than that required by theory, and to dissolve it in less water than is needed for the finished solution. This solution is titrated, its strength determined and then diluted to the proper measure.

After dilution it should be again carefully titrated and its titer verified.

All volumetric solutions should be made with distilled water and with reagents which are of a high degree of purity.

Standard Temperature. A cubic centimeter is the volume occupied by one gram of distilled water at its maximum density 4° C. (39° F.). This, however, is not the cubic centimeter

used in volumetric analysis. It is convenient to use in analyses of this sort a cubic centimeter which represents the volume of one gram of distilled water at a temperature which is easily attained and maintained at any season of the year.

The temperature at which measuring instruments are graduated is the temperature at which volumetric solutions should be prepared, and at which all volumetric operations should be conducted. 4° C. is a temperature at which it is obviously impossible to work except during one or two months of the year. For this reason the temperature of 16° C. (60.8° F.) has been taken as the standard. The cubic centimeter used in volumetric analysis, under this standard, is the volume occupied by one gram of distilled water at the latter temperature.

The employment of this standard of temperature, though long in vogue, is justly criticized as too low. In order to obtain accurate results the temperature of the atmosphere in which the titration is performed must not be too much at variance with the temperature at which the instruments are graduated and the solutions made. A temperature of 16° C. is one which is exceedingly difficult to maintain in the warm months of the year, therefore it has been suggested to take a higher temperature as the standard.

The U.S.P. VIII recommends the employment of 25° C. (77° F.) as the standard. This, while better than the lower temperature, is regarded by many as being too high and the use of 20° C. (68° F.) as the standard is now being very favorably considered, this being nearer the average temperature of the atmosphere in laboratories throughout the year. What ever temperature is adopted, it is at this temperature that the whole set of measuring instruments must be graduated, and all titrations carried out. It would be obviously improper to use a burette graduated at 16° C. and a flask or cylinder

graduated at 25° C., or to employ solutions at a temperature which is different from that at which they are made.

Mil. The term cubic centimeter (cc.) has been replaced by the word mil in the U. S. P. IX, and in many other recent books. The United States Bureau of Standards declared that the term cubic centimeter was a misnomer, there being a slight difference between the thousandth part of a liter and the cubic centimeter, as one liter was determined to be equivalent to 1.000027 cubic decimeters. Hence the word mil, an abbreviation of milliliter, was adopted and represents the thousandth part of a liter.

The U. S. P. liter is the volume occupied by 996.04 gms. of distilled water, weighed in air with brass weights at a temperature of 25° C. and barometric pressure of 760 mm.

To Titrate a substance means to test it volumetrically for the amount of pure substance it contains. The term is used in preference to "tested" or "analyzed," because these terms may relate to qualitative examinations as well as quantitative, whereas titration applies only to volumetric analysis.

Residual Titration, Re-titration, sometimes called Back Titration, consists in treating the substance under examination with standard solution in a quantity known to be in excess of that actually required; the excess (or residue) is then ascertained by residual titration with another standard solution.

Thus the quantity of the first solution which went into combination is found.

Example. Ammonium carbonate is treated first with $\frac{N}{1}$ H_2SO_4 in excess, and the excess then found by titration with $\frac{N}{1}$ KOH.

The quantity of the $\frac{N}{1}$ KOH used is then deducted from the quantity of $\frac{N}{1}$ H_2SO_4 added, which gives the quantity of the latter which was neutralized by the ammonium carbonate.

Titrations may be carried out in flasks, beakers, or in white porcelain evaporating dishes. Flasks of the Erlenmeyer pattern, see Fig. 24, having a short narrow neck and a broad flat bottom, are very desirable for this purpose; they admit of shaking their contents without danger of loss, and permit ready observation of color changes. If a flask is used the tip of the burette should extend well into its neck in order to prevent any loss of the reagent. The flask should be rotated after each addition of the reagent, and when the end of titration is near, any of the solution adhering to the sides of the flask should be washed down with distilled water. A white porcelain tile, or a sheet of white paper placed under the flask or beaker, aids materially in the observation of the color change.

CHAPTER IV

INDICATORS.*

In volumetric analysis the substance to be analyzed in the state of solution is placed in a beaker and the standard solution is added from a burette until a certain reaction is produced. The exact moment when a sufficient quantity of the standard solution has been added is known by certain visible changes, which differ according to the substance analyzed and the standard solution used. When such a visible change occurs the " end-reaction " is reached.

The end-reaction manifests itself in various ways, as follows:

1. Cessation of precipitation.
2. First appearance of a precipitate.
3. Change of color.

In some cases, however, the addition of the standard solution to the substance under analysis does not produce either a precipitate or a change of color; in such cases we must resort to the use of an indicator.

An indicator is a substance which is used in volumetric analysis, and which indicates by change of color, or some other visible sign, the exact point at which a given reaction is complete.

Generally the indicator is added to the substance under examination, but in a few cases it is used alongside, a drop of the substance being occasionally brought in contact with a drop of the indicator.

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* A more detailed description of the individual indicators is given in the Appendix.

Thus in estimating an alkali with an acid volumetric solution the alkali is shown to be completely neutralized when the litmus tincture which was added becomes faintly red or the phenolphthalein colorless. Again, when haloid salts are estimated with nitrate of silver solution, chromate of potassium is added as indicator. A white precipitate is produced as long as any halogen is present to combine with the silver, and when all is precipitated the chromate of potassium acts upon the silver nitrate, forming the red silver chromate, this color thus showing that all the halogen has been precipitated.

INDICATORS COMMONLY USED

The principle indicators used are:

Tincture of Litmus, which shows acidity by turning red and alkalinity by becoming blue.

Phenolphthalein Solution, which is colorless in acid solutions and red in alkaline solutions, but is not reliable for alkaline phosphates, bicarbonates or ammonia.

Methyl-orange Solution turns red with acids and yellow with alkalies. It is not affected by carbonic acid, and is therefore adapted for the titration of alkaline carbonates.

Rosolic-acid Solution is yellow with acids and violet-red with alkalies. It is very sensitive to ammonia.

Tincture of Turmeric turns brown with alkalies, and the yellow color is restored by acids.

Cochineal Solution turns violet with alkalies and yellowish with acids. It is used chiefly in the presence of ammonia or alkali earths.

Eosin Solution is red by transmitted light, and shows a strong green fluorescence by reflected light. Acids destroy this fluorescence and alkalies restore it.

Brazil-wood Test-solution turns purplish-red with alkalies and yellow with acids.

Fluorescein Test-solution shows a strong green fluorescence by reflected light in the presence of the least excess of an alkali.

Neutral Potassium-chromate Test-solution is used in the titration of haloid salts with silver-nitrate solution. It indicates that all the halogen has combined with the silver by producing a red-colored precipitate (silver chromate).

Potassium-ferricyanide Test-solution is used in the estimation of ferrous salts with potassium-dichromate solution. It gives a blue color to a drop of the solution on a white slab as long as any iron salt is present which has not been oxidized to ferric.

THE IONIZATION OR DISSOCIATION THEORY

When a soluble salt dissolves in water, its molecules split up or dissociate more or less completely into parts called *ions*. This behavior of substances, on going into solution, is known as electrolytic dissociation or ionization.

Ions are electrically charged atoms or groups of atoms and are of similar composition to the substanecs formed from the compound when an electric current is passed through the solution. The electro-positive ions migrate to and collect around the negative pole (cathode) and hence are called cathions, while the electro-negative ions are called anions, because they concentrate around the positive pole or anode. The dissociation of a compound into its ions when an electric current is passed through its solution, although spoken of as electrolytic dissociation, is really not caused by the electric current, since the dissociation into ions occurs at once upon dissolving the substance in water and without the aid of an electric current, the action of the current being the transportation of the separated ions to the poles.

The dissociation of compounds into ions when dissolved in water is illustrated in the following list:

Sodium chlorid into . . . . . (Na+) and (Cl−)
Potassium nitrate into . . . . . (K+) " (NO_3−)
" hydroxid into . . . . . (K+) " (OH−)
" acetate into . . . . . (K+) " ($C_2H_3O_2$−)
Sulphuric acid into . . . . . (H+) " (HSO_4−)
or (H+) " (H+) and (SO_4)

The extent of this dissociation depends upon the nature of the substance and the degree of dilution; the greater the dilution the more complete the dissociation. Furthermore, strong acids and bases dissociate readily, even in comparatively concentrated solutions, while the weaker acids and bases are more or less undissociated when dissolved, i.e., they are not readily split up into ions. Their salts, however, are immediately and completely ionized. Therefore, upon neutralizing a weak acid or base, an ionizable salt is formed. According to the theory of Arrhenius, the reactions of analytical chemistry are chiefly reactions between ions and not between atoms.

Strong acids, bases and salts exist in solution, not as molecules but chiefly in the form of ions. The formation of silxer chlorid by the reaction between silver nitrate and sodium chlorid takes place according to the following equation:

$$\overset{+}{Ag}/\overset{-}{NO_3}Aq. + \overset{+}{Na}/\overset{-}{Cl}Aq. = AgCl(\text{ solid}) + \overset{+}{Na}/\overset{-}{NO_3}Aq.$$

The state of dissociation being denoted by the vertical line between the ions of the molecules.

This theory also explains why $\overset{+}{K}/ClO_3$ with $\overset{+}{Ag}/\overset{-}{NO_3}$ does not form AgCl, in that the reaction involves the ion $\overset{-}{ClO_3}$ and not the atom Cl.

Theories of Indicators. In connection with the use of indicators in neutralization analyses, the question as to the cause of the color changes is one of considerable interest.

Two distinct views are held. Of these the *Ionization Theory of Ostwald* has received almost universal acceptance. According to this theory the color changes are ascribed to a change in the indicator from a molecular to an ionic condition. As exemplified in the case of phenolphthalein the colorless molecule

$$OCOC_6H_4C-(C_6H_4OH)_2 \quad . \quad . \quad . \quad . \quad (I)$$

is dissociated into the red negative ion

$$OCOC_6H_4C\cdot(C_6H_4OH)C_6H_4\bar{O}. \quad . \quad . \quad . \quad (II)$$

In the other and less known view on this subject (the *Chromophoric Theory*),* the sensitiveness of the indicators and its color changes is ascribed to a change in the constitution of the indicator, involving a chromophoric group, under the influence of hydrogen and hydroxyl ions. According to this view the color change is due (in the case of phenolphthalein) to a change of constitution from the colorless lactoid (I) with no chromophoric group, to the colored quinoid (III) with a quinone chromophore.

$$(NaOOC\cdot C_6H_4)(HOC_6H_4)C:C_6H_4:O, \quad . \quad . \quad (III)$$

and that the ionization of the sodium salt is merely a coincidence and not the cause of the color change.

Whichever of these views is the correct one, remains for future investigations to prove. That of Ostwald, being most generally accepted at the present time, is treated more fully below.

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* See Julius Stieglitz, Jour. Am. Chem. Soc., XXV, 1112 (1903).

The Ionization Theory of Indicators.* The indicators used in alkalimetry and acidimetry are compounds of feeble acid or basic character, and hence not prone to dissociation in solution, but when neutralized the salt formed ionizes the instant of its formation; the ions so liberated give rise to colors which differ from those of the original compounds.

Any feeble acid or base may be utilized as an indicator if its ions have a color different from that of the un-ionized compound. Strong acids or bases are not suited as indicators, because they ionize while in a free state on dilution, and thus give no color when neutralized.

A solution in which H ions predominate has an acid reaction, while one in which OH ions predominate reacts alkaline.

Phenolphthalein is a feebly acid indicator, and in its undissociated state is colorless. It does not dissociate readily unless neutralized, but when sodium hydroxid is added to its solution, a sodium salt of phenolphthalein is formed which immediately ionizes and the ions liberated impart to the solution a brilliant red color. If now some acid is added the sodium salt is decomposed and the acid phenolphthalein again set free, and the solution becomes colorless.

If a few drops of phenolphthalein solution be added to an acid solution, ionization of the former is prevented by the presence of the stronger acid; if now some sodium hydroxid solution is added, the OH ions of the latter unite with the H ions of the acid, and when the acid is completely neutralized the first drop of excess of alkali unites with the phenolphthalein, forming a salt which immediately ionizes and produces the characteristic red color which shows the end of the reaction.

In the titration of a feeble acid the end-point is often

* See Ostwald's "Lehrbuch der Allgemeinen Chemie," 1891, and "Scientific Foundations of Analytical Chemistry," 1900; also Walker's "Introduction to Physical Chemistry," 1899.

indistinct and is lacking in sharpness; this is because the indicator used has a greater tendency to ionize than the acid itself. In this case the H ions present just before the completion of the reaction are not in sufficient amount to fully retard the ionization of the indicator, and hence the latter dissociates partly before neutralization is complete and gives rise to an indefinite end-reaction. Therefore it is necessary when titrating a feeble acid that an indicator should be selected whose alkali salt ionizes with the production of a distinct color change, and whose tendency to ionize is less than that of the acid. Phenolphthalein is a suitable indicator in this case, provided a strong alkali be used for titrating.

Fixed alkalies readily yield ionizable salts with phenolphthalein, but ammonia does not. The latter being too weak a base to yield with so feeble an acid, a salt which can withstand the hydrolytic action of the water in dilute solutions, and as a consequence a larger excess of the ammonia must be used to overcome this. Thus is accounted for the imperfect color change of phenolphthalein when ammonia or its salts are present and why the color becomes visible only after a large excess of the alkali is added.

Paranitrophenol is also an acid indicator; it exists in solution in the form of undissociated colorless molecules, yet its electro-negative ion is intensely yellow in color. This compound has a slight tendency to dissociate in dilute solutions, but the presence of a trace of a stronger acid will overcome this tendency and the solution remains colorless. If an alkali is, however, added, a salt of paranitrophenol is formed which immediately ionizes and exhibits the intense yellow color of its liberated ion.

Other indicators exhibit a color in both the ionized and the non-ionized state, but the colors in both conditions are different, as in the case of litmus, lacmoid and methyl orange.

Methyl orange is both an acid and a base and will form ionizable salts with either acids or alkalies; its indicator characteristics are, however, due essentially to its basic character.

The salt which methyl orange forms with acids dissociates into red ions; this, upon the addition of an alkali, returns to its undissociated state, which is yellow. Because of its weak basic character its compound with acids is readily decomposed by alkalies, but it takes a strong acid or a relatively large quantity of a feeble acid to dissociate it in its non-ionized state, hence this indicator is very sensitive to alkalies, and much less so to acids.

With reference to the acid character of the indicator the explanation of its action is that the non-ionized indicator is red, while its ion is yellow. Acids lessen its ionization and produce a red color, while alkalies produce a highly ionizable salt and hence a yellow color. When a weak but slightly ionizable acid is added to the methyl orange solution, the $H^{\cdot}$ ions of the acid given up in excess of the amount required for neutralization are not sufficient to yield enough of a non-ionizable salt to produce a decided red color, hence a large quantity of such a weak acid is required to give an acid indication. This would explain why methyl orange is not suitable as an indicator for weak acids, and why it is very sensitive to alkalies.

Litmus is an acid indicator which slightly dissociates in solution. Its non-ionized molecules are red, but its negative ions are blue. If it is added to an alkali, a salt is formed which at once ionizes and gives a blue color. If added to an acid, ionization is prevented and the red color of the non-ionized molecules appears.

From the above explanations it will be seen that indicators cannot be indiscriminately used, and that no one indicator

will be suitable for every titration. Hence the indicator must be selected to suit each case. This selection is facilitated by reference to the classification of indicators, according to F. Glaser, Ztchr. f. a. Chem., 1899, 273+.

Group I. **Indicators Forming Fairly Stable Salts.** The members of this group comprise such indicators as are (1) of a strong acid character and which react readily with weak bases, or (2) of a feeble basic character and which require a strong acid to form a stable salt. Hence they will be found to be very *sensitive to alkalies*, and are useful in the titration of weak bases, as ammonia and the amine bases, as well as strong bases and acids. The indicators of this group are the following, arranged in the order of their sensitiveness towards alkalies:

(1) Iodeosin, Resazurin; (2) Tropæolin OO, Luteol; (3) Methyl and Ethyl Orange; (4) Congo Red; (5) Cochineal; (6) Lacmoid.

Group II. **Indicators Possessing Faint Acid Properties and Yielding Salts which are Very Unstable.** These are readily decomposed by relatively feeble acids, and are in consequence *very sensitive towards acids*, slightly so towards alkalies.

They are: (1) Rosolic acid; (2) Curcuma; (3) Phenolphthalein, Flavescin; (4) Alpha-naphtholbenzein.

Group III. **Indicators Occupying a Place Midway between the Other Two Groups.** They are somewhat stronger acids than those of Group II, but feebler than those of Group I.

They are fairly sensitive towards both acids and alkalies, but are more sensitive towards acids than those of Group I, and less so towards alkalies. They are:

(1) Fluorescein, Phenacetolin; (2) Hæmatoxylin, Galleïn, Alizarin; (3) Litmus; (4) Paranitrophenol.

This division of indicators into groups, as above, facilitates the selection of an indicator suitable for the work in hand.

For instance, for titrating weak acids, a glance at the groups will show that the members of Group II are best adapted for this purpose. Again, weak bases will be best titrated by the indicators of Group I. Strong acids or bases may be titrated by means of any of the indicators.

The quantity of indicator taken in a titration is a matter of considerable moment. The smallest quantity which will produce a distinct color should be taken, but it is equally important that the quantity be not too small for the volume of liquid; for in high dilutions the hydrolytic action of water asserts itself, and intermediate tints will result, which interfere with the sharpness of the end color.

If too much of the indicator is used, the sensitiveness is lessened, because acid or alkali must be added to convert the indicator into a salt, or when formed to decompose it; i.e., a minimum of excess of the titrating fluid would react with a small portion only of the indicator and intermediate tints would be produced, until sufficient of the titrating solution has been added to neutralize all of the indicator present. This is especially true when using centinormal solutions. 20 drops of litmus added to 10 mils of water require from 10 to 14 drops of $\frac{N}{100}$ acid or alkali solution to produce a change of color. Thus the indicator itself takes up some of the standard solution, and hence the necessity for using as small a quantity of the indicator as possible; usually from *3 to 5 drops of the indicator may be taken to each 50 or 100 cc. of the fluid titrated.*

The degree of dilution of the substance titrated is also a matter of considerable moment. In very concentrated solutions ionization does not so readily occur, while too great a dilution diminishes the reactive ability of the ions because of their greater separation, and also because of the hydrolytic dissociation of water itself into $H^{\cdot}$ and OH ions which

react acid and alkaline respectively, and which brings about a premature dissociation of the indicator.

The Requirements of a Good Indicator, according to H. A. Cripps, are:

I. The end-reaction should be marked by a prominent change of color.

II. The smallest possible quantity of the reagent should be required to effect this change.

III. High tintorial power, which of itself assists in the fulfilment of the second requirement, less of the indicator being required.

IV. The change of color should not be affected by the impurities commonly present in the substance under examination, nor by the products of the reaction.

In addition to these requirements it is a distinct advantage if the color reaction is equally decided in alcoholic as in aqueous liquids.

A GUIDE FOR THE SELECTION OF INDICATORS

For Hydroxids and Carbonates

Indicators not affected by CO_2 (Cold Titrations)	**Indicators affected by CO_2** (Hot Titrations)
Methyl Orange, Galleïn, Phenacetolin, Congo Red, Iodeosin, Cochineal.	Phenolphthalein (useless in presence of NH_3 or its salts), Lacmoid, Rosolic Acid, Resazurin.

For Ammonia (NH_3)	For Ammonium Carbonate
Rosolic Acid, Methyl Orange, Congo Red, Litmus, Galleïn.	Same indicators as for ammonia, also Phenacetalin and Phenolphthalein.

For Inorganic Acids

H_2SO_4, HCl, HNO_3.

Phenolphthalein, Litmus, Rosolic Acid, Methyl Orange.

H_3PO_4.

Phenolphthalein (neutralized to Na_2HPO_4).

Methyl Orange and Cochineal (each neutralized to NaH_2PO_4).

H_2SO_3.

Rosolic Acid and Methyl Orange.

H_3BO_3.

Phenolphthalein (after addition of glycerin), Litmus and Turmeric paper.

For Organic Acids

Phenolphthalein (all) Rosolic Acid (except acetic, citric and tartaric), Galleïn.

CHAPTER V

APPARATUS USED IN VOLUMETRIC ANALYSES

The Burette is a graduated glass tube which holds from 25 to 100 mils and is graduated in fifths or tenths of a mil. and provided at the lower end with a rubber tube and pinch-cock. The use of this instrument is to accurately measure quantities of standard solutions used in an analysis. It is in an upright position when in use, and the flow of the solution can be regulated so as to run out in a stream or flow in drops by pressing the pinch-cock between the thumb and forefinger. The quantity of solution used can be read from the graduation on the outside of the tube. This is the simplest and most common form of burette, and is known as *Mohr's* (Fig. 1).

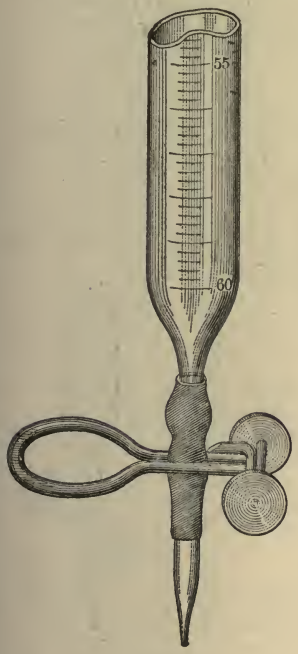

FIG. 1.

The use of the pinch-cock in Mohr's burette may be dispensed with by introducing into the rubber tube a small piece of glass rod, which must not fit too tightly. By firmly squeezing the rubber tube surrounding the glass rod a small canal is opened, through which the liquid escapes. A

very delicate action can in this way be obtained, and the flow of the liquid is completely under the control of the operator. (See Fig. 2.)

The greatest drawback to this burette is that it cannot be used for permanganate or other solutions that act upon the rubber.

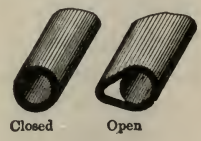

FIG. 2.

This defect can be overcome by the use of a burette having a glass stop-cock in place of the rubber tubing and pinch-cock. This form has the additional advantage of being capable of delivering the solution in drops while both hands of the operator are disengaged (Fig. 3).

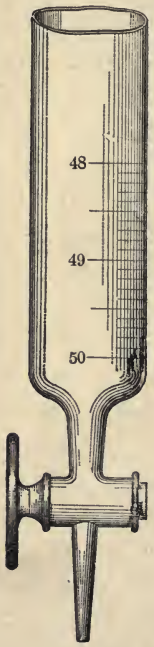

FIG. 3.

Another good arrangement is that in which the tap is placed in an oblique position, so that it will not easily drop out of place (Fig. 4).

These glass stop-cock burettes should be emptied and washed immediately after use, especially if soda or potassa solution has been used; for these act upon the glass and often cause the stopper to stick so firmly that it cannot be turned or removed without danger of breaking the instrument.

FIG. 4.

The most satisfactory form of glass stop-cock is that shown in Fig. 5.

When a number of estimations are to be made in which the same volumetric solution is employed, the arrangement shown in Fig. 6 is very serviceable.

A T-shaped glass tube is inserted between the lower end of the burette and the pinch-cock and connected by a rubber tube with a reservoir containing the volumetric solution.

The tube which communicates with the reservoir is provided with a pinch-cock, which, when open, allows the solution to flow into and fill the burette in so gradual a manner that

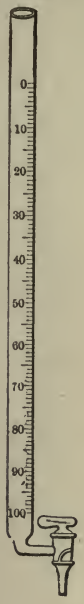

Fig. 5.

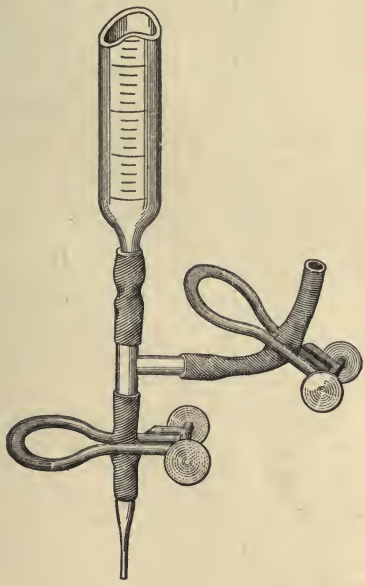

Fig. 6.

no bubbles are formed. The burette is emptied in the usual manner.

E. & A. Automatic Burette (Fig. 7). This is used for the same purpose as the foregoing. It is provided with a side tube for connection with reservoir, and has an overflow cup which prevents its being filled to above the zero mark. The three-way stop-cock is so arranged that if turned one

way the inlet is opened and the liquid from the reservoir flows into and fills the burette. If turned the other way the inlet is closed and the outlet is opened and the burette may be

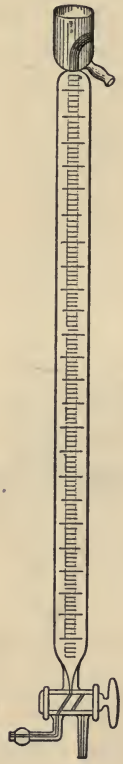

Fig. 7.

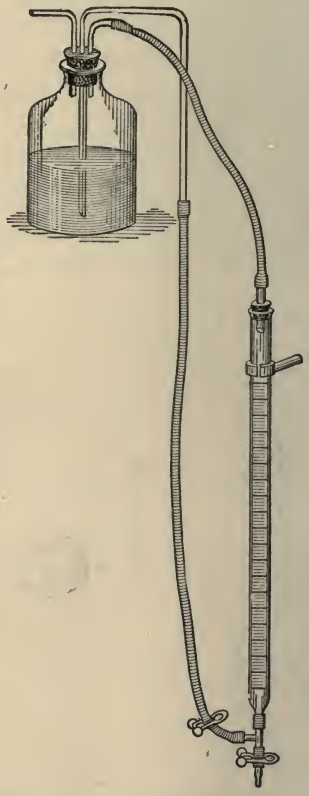

Fig. 8.

emptied. If the handle of the stop-cock is turned half-way round, both openings are closed.

There are many other forms of automatic burettes.

When working with solutions which are readily altered by contact with air, as for example, stannous chlorid, potas-

sium, sodium, or barium hydroxid or ammonia, an arrangement like that depicted in Fig. 8 is very serviceable. In this the upper end of the burette is connected with the reservoir by means of a rubber tube, thus making an air-tight combination between the burette and the reservoir. Its utility may be further enhanced by providing the reservoir with a soda-lime tube or some other suitable absorption tube.

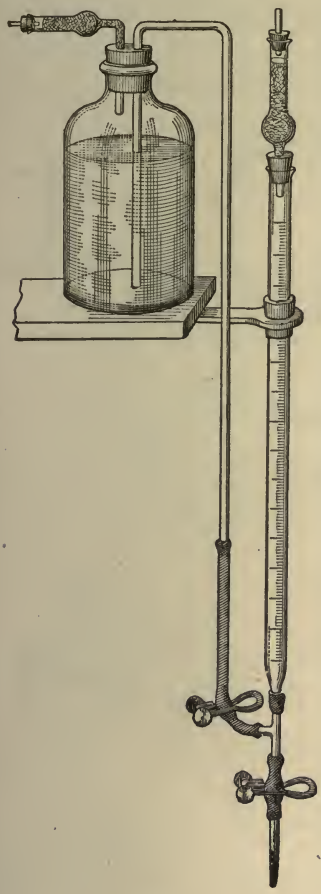

Fig. 9.

Another form of apparatus is shown in Fig. 9. In this both the burette and the reservoir are provided with tubes containing soda-lime to insure a protection against the admission of CO_2 and moisture from the air.

Pinch-cocks used with Mohr's burettes are of various kinds. See Figs. 10, 11 and 12.

The screw pinch-cock,* Fig. 12, is a very useful device; it may be used like the ordinary pinch-cock by pressure with the fingers upon *a–a*, when a rapid flow is desired, or the nut-screw (*b*) may be so adjusted as to allow a slower flow or to deliver the solution in drops, thus giving the operator the freedom of both hands for other work.

Burette supports are of various forms. One of the best

* W. v. Hergendorf.

for one or two burettes is shown in Fig. 13. It is made of iron, can stand firmly upon an uneven surface, and does not easily tip over. The burettes are fastened to it by means of clamps, illustrated in Figs. 14 and 15.

A revolving burette-holder for eight burettes is shown in

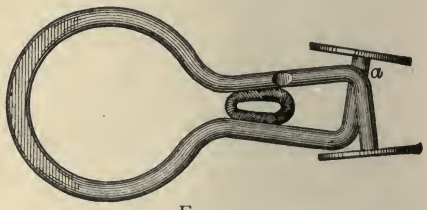

FIG. 10.

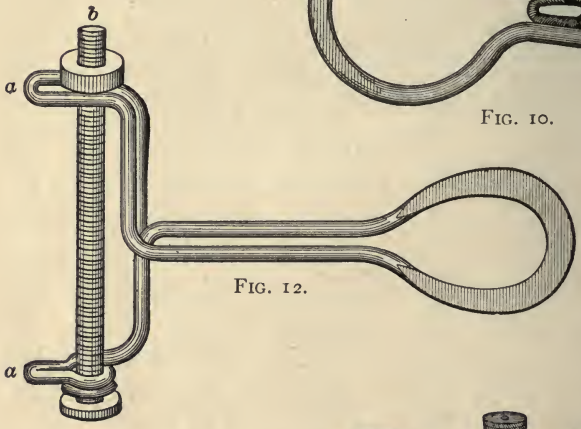

FIG. 12.

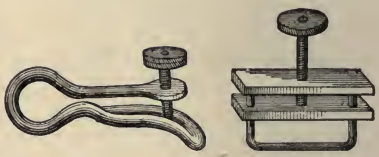

FIG. 11.

Fig. 16. Burrette-supports are also made with white porcelain base, which enables the operator more readily to see the change of color in the liquid titrated.

Pipettes are of two kinds—those which are marked to deliver one quantity only, and those which are graduated on the stem like burettes. Their use is to measure out portions of solutions with exactness.

Pipettes are filled by applying the mouth to the upper end and sucking the liquid up to the mark, then, by closing the upper opening with the forefinger, the liquid is prevented from running out, but may be delivered in drops or allowed to run out to any mark by lessening the pressure of the finger over the opening.

In using the pipettes of the first class (Fig. 17) the finger

Fig. 13.

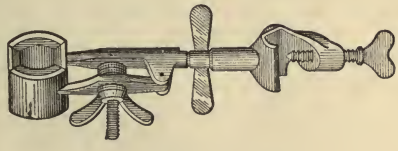

Fig. 14.

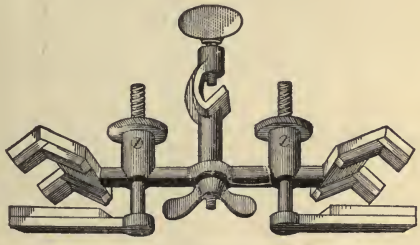

Fig. 15.

is raised and the instrument allowed to empty itself entirely. A drop or two, however, usually remains in the lower portion of the instrument, which may be blown out, though this is not considered good practice. By inclining the pipette and placing the point against the side of the vessel which is to receive the liquid, the instrument may be emptied more satisfactorily.

Pipettes of the second class (Fig. 18) are never emptied completely when in use. The flow of the liquid is regulated by the pressure of the finger over the upper opening, and stopped at the desired point.

A very convenient form of pipette is one which has attached to its upper end a piece of rubber tubing, into which a short piece of glass rod has been inserted. By squeezing the

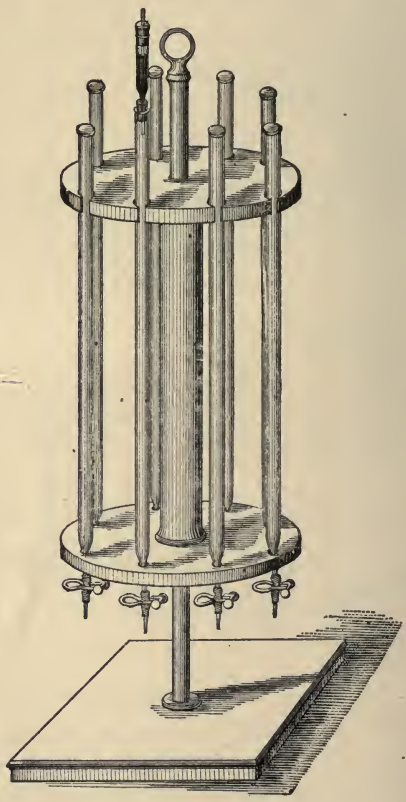

Fig. 16.

rubber surrounding the glass rod firmly between the fingers, a canal is opened and the liquid can be drawn up into the pipette by suction with the lips and run out again. By removing the pressure the canal closes and the flow of the liquid is stopped at any point (Fig. 19).

The Nipple Pipette is very convenient for measuring small quantities of liquids, such as 1 or 2 mils (Fig. 20).

When a volatile or highly poisonous solution is to be measured it is not advisable to suck it up with the mouth.

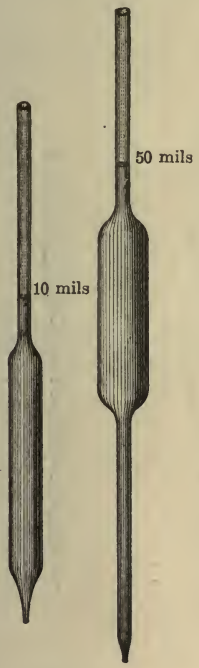

FIG. 17.

FIG. 18.

FIG. 19.

The pipette in this case is filled by dipping it into the liquid contained in a long, narrow vessel, until the liquid reaches the proper mark on the pipette, then closing the upper opening and withdrawing. When this is done the liquid which adheres to the outside of the pipette should be dried off before the measured liquid is delivered.

A French firm has introduced pipettes provided with suction

pumps, shown in various forms by Fig. 21, which possess the advantage over the ordinary forms provided with a compressible rubber bulb, that the liquid can with perfect ease be drawn up to the desired point on the scale, and with absolute accuracy maintained at the same height as long as may be desired.

The Measuring-flask is a vessel made of thin glass having

Fig. 20.

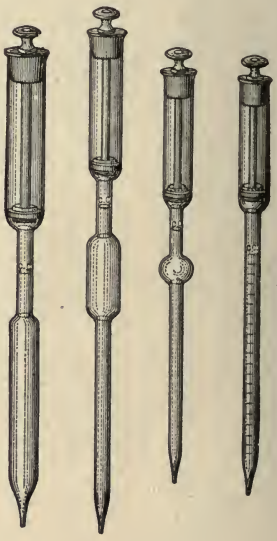

Fig. 21.

a narrow neck, and so constructed as to hold a definite amount of liquid when filled up to the mark on the neck. These flasks are of various sizes, holding 100, 250, 500 1000 mils, etc., but are generally called "*Liter Flasks.*" (Fig. 22.)

Liter flasks are used for making volumetric solutions.

Those which have the mark below the middle of the neck are to be preferred, because the contents can be more easily shaken.

Liter flasks are sometimes made with two marks on the neck very near together; the lower one is the liter mark. If the flask is required to deliver a liter, it must be filled to the upper mark, the difference between the two measures being

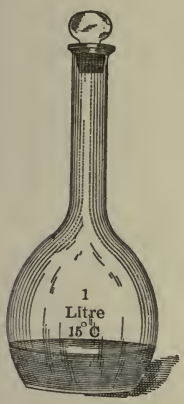

Fig. 22.

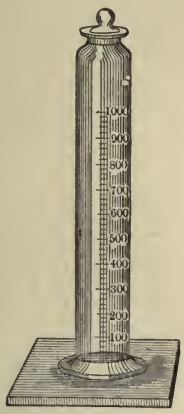

Fig. 23.

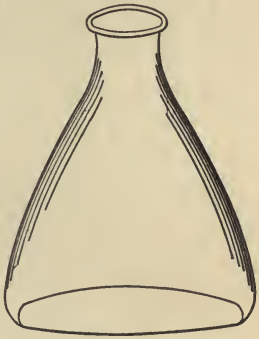

Fig. 24.

the equivalent of the liquid which remains in the flask adhering to the sides.

The Test-mixer, or **Graduated Cylinder** (Fig. 23) is for measuring and mixing smaller quantities of solutions. They are made of different sizes, holding 100, 250, 500 and 1000 mils, and graduated in fifths or tenths of a mil.

Titration Flasks. Titrations may be carried out in flasks of any usual shape, or in beakers, or evaporating dishes, but the flask illustrated in Fig. 24 is to be preferred.

CHAPTER VI

ON THE USE OF APPARATUS

It is important that all apparatus used in volumetric analysis be perfectly clean. Even new apparatus should be cleansed by passing dilute hydrochloric acid through them and then rinsing with distilled water.

If the burette, pipette, or other instrument is even slightly greasy, the liquid will not flow smoothly, and drops of the liquid will remain adhering to the sides, thus leading to inaccurate results.

Greasiness may be removed with dilute soda solution. If this fails the instrument should be allowed to remain for some little time in a solution containing sulphuric acid and potassium dichromate, which will radically remove all traces of grease.

The burette or other measuring instruments should never be filled with volumetric solution without first rinsing, even if the burette be perfectly dry.

It is well to wash the inside of the instrument with two or three small portions of the solution with which it is to be filled.

The burette may be filled with the aid of a funnel, the stem of which should be placed against the inner wall of the burette, so that the solution will flow down the side and thus prevent the formation of bubbles.

The burette should be filled to above the zero mark, and the air-bubbles, if there are any, removed by gently tapping with the finger.

A portion of the liquid should then be allowed to run out in a stream so that no air-bubbles remain in the lower part of the burette. In the glass tap burette it can be easily seen if any air is present, but in the pinch-cock burette it is sometimes necessary to take hold of the rubber tube between the thumb and forefinger and gently stroke upward. Or the glass nip at the lower end of the burette may be pointed upward, and the pinch-cock opened wide so that a stream of the liquid will pass through and force out any air that may be inclosed.

If the titration is to be conducted at a high temperature, as in the estimation of carbonates, when litmus is used as the indicator, or in the estimation of sugar by copper solution, a long rubber tube should be attached to the lower end of the burette. The boiling can then be done at a little distance, and the expansion of the liquid in the burette avoided. The pinch-cock is fixed about midway on the tube.

Hart calls attention to the fact that if the fluid in a burette or pipette be run out rapidly at one time and slowly at another, different amounts of fluid are obtained.

This is due to the adhesion of the fluid to the inner sides of the instrument, and reading before it has settled down. It is therefore advisable always to deliver burettes slowly, as more constant results are then obtained.

Solutions which are measured by means of pipettes should be dilute, since concentrated solutions adhere to glass with different degrees of tenacity, and hence the amount of fluid delivered is slightly less than that measured.

The temperature of the solutions measured should be taken into account, since all liquids are affected by change of temperature, expanding and contracting as the temperature is increased or reduced.

This change of volume in the case of standard solutions does not exactly correspond to that in pure water; in fact,

some of them differ widely. The correction of the volume of a standard solution for the temperature by the expansion coefficient of water is not entirely satisfactory, but in the case of very dilute solutions this may be done.

Casamajor (C. N., xxxv, 160) gives the following figures showing the relative contraction and expansion of water below and above 15° C.:

Degrees C.	Degrees C.
8 − .000590	17 + .000305
9 − .000550	18 + .000473
10 − .000492	19 + .000652
11 − .000420	20 + .000841
12 − .000334	21 + .001039
13 − .000236	22 + .001246
14 − .000124	23 + .001462
15 − normal	24 + .001686
16 + .000147	25 + .001919

By means of these numbers it is easy to calculate the volume of liquid at 15° C. corresponding to any volume observed at any temperature between 8° C. and 25° C. If 25 cc. of solution had been used at 20° C., the table shows that 1 cc. of water passing from 15° to 20° is increased to 1.000841 cc. Therefore, by dividing 25 cc. by 1.000841, the quotient, 24.97 cc. is obtained, which represents the volume at 15° C. corresponding to 25 cc. at 20° C.

These corrections are of value only for very dilute solutions and for water, but useless for concentrated solutions. Slight variations of atmospheric pressure may be disregarded.

ON THE READING OF INSTRUMENTS

In narrow vessels the surface of liquids is never level. This is owing to the capillary attraction exerted by the sides of the vessel upon the liquid, drawing the edge up and forming

a saucerlike concavity (Fig. 25). All liquids present this concave surface except mercury, the surface of which is convex.

This behavior of liquids makes it difficult to find a distinct level, and in reading the measure either the upper meniscus (*a*) or the lower meniscus (*b*) may be used (Fig. 26).

The most satisfactory results are obtained if the lowest point of the curve (*b*) is used, especially with light-colored

Fig. 25.

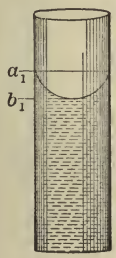

Fig. 26.

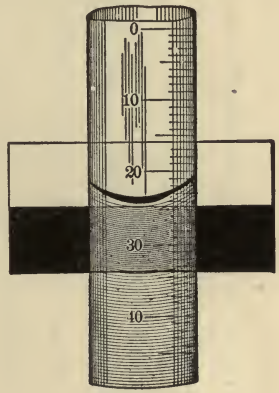

Fig. 27.

solutions. But if dark-colored or opaque solutions are measured it is necessary to use the upper meniscus (*a*) for reading.

In all cases the eye should be brought on a level with the surface of the liquid in reading the graduation.

The eye is very much assisted by using a small card, the lower half of which is black and the upper half white, This card is held behind the burette, the dividing line between white and black being about an eighth of an inch below the surface of the liquid. The eye is then brought on a level with it, and the lower meniscus can be distinctly seen as a sharply defined black line against the white background (Fig. 27).

Erdmann's Float, Fig. 28, is an elongated glass bulb, which is weighted at its lower end with mercury, to keep it in an upright position when floating. It is of such diameter that

FIG. 28.

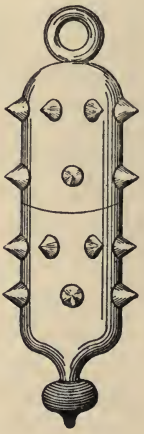

FIG. 29.

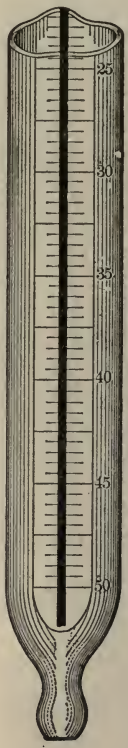

FIG. 30.

it will slide easily up and down inside of a burette. There is a ring at the top by which it can be lifted in or out by means of a bent wire. Around its center a line is marked. At this line instead of at the meniscus the reading is taken.

These floats are sometimes provided with a thermometer, and they then register the temperature as well as the volume.

Others are provided with projecting points along the sides,

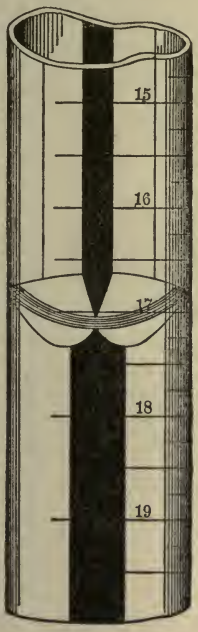

FIG. 31.

FIG. 32.

the object of which is to prevent it from adhering to the walls of the burette. (See Fig. 29.)

For the purpose of facilitating the reading, special forms of burettes are constructed which are provided with a dark longitudinal stripe on a white enameled background (Fig. 30); the reflection of the dark stripe with the meniscus produces the peculiar appearance shown in Fig. 31. The narrowest point is at the middle of the meniscus, and by reading from this point very accurate measurements are obtained. The

same effect can be produced by holding behind an ordinary burette a white flexible card having a heavy black longitudinal stripe, about one-eighth inch in width.

Another form of burette designed for the purpose of facilitating reading is that provided with white enameled sides, leaving a strip of clear glass in front and back (Fig. 32). This form is especially adapted for use with dark-colored liquids, such as iodin and permanganate.

CALIBRATION OF INSTRUMENTS

Burettes are made from tubes of nearly uniform width. They are filled with distilled water at 15° C.* (59° F.) to the 0 mark, and then 25, 50 or 100 cc. run out, and another mark made at the surface of the liquid. The distance between these two marks is then divided into 25, 50 or 100 equal parts, and the spaces again subdivided into fifths and tenths. Now it is very rarely possible to obtain tubes of exactly the same caliber throughout, and the divisions made as above do not always represent exactly what they are intended to.

If the tube is wider at one point the divisions at that point will contain more, and if it is narrower they will contain less than they should.

Hence before using a new burette, or in fact any other measuring instrument, it is essential that the error, if any, should be determined. This is done as follows:

Fill the burette to the 0 mark with distilled water at 15° C. (59° F.) and run out 10 cc. at a time into a small weighed flask, and weigh after each addition of 10 cc.

Each 10 cc. should weigh exactly 10 gms., and every

* Instead of 15° C. (59° F.) the temperature 25° C. (77° F.) is recommended because this more nearly approaches the ordinary temperature of the atmosphere in temperate climes.

deviation found should be noted and taken into consideration in using the instrument.

Example

Flask weighed 20.0000 grams.
" +10 cc. " 30.1005 "
" +20 cc. " 40.0499 "
" +30 cc. " 49.8000 "
" +40 cc. " 59.9700 "
" +50 cc. " 70.0100 "

Thus the 1st 10. cc weighed 10.1005 grams.
2d 10 cc. " 9.9494 "
3d 10 cc. " 9.7501 "
4th 10 cc. " 10.1700 "
5th 10 cc. " 10.0400 "

Having obtained these data, a table like the following may be constructed and kept in some convenient place where it can be readily consulted whenever the burette it represents is being used. It is not necessary to carry the figure beyond the second decimal place.

No. of cc. as read on burette.	No. of cc. as corrected.	No. of cc. as read on burette.	No. of cc. as corrected.	No. of cc. as read on burette.	No. of cc. as corrected.
1	1.01	14	14.06	27	26.79
2	2.02	15	15.05	28	27.76
3	3.03	16	16.04	29	28.73
4	4.04	17	17.03	30	29.70
5	5.05	18	18.02	31	30.71
6	6.06	19	19.01	32	31.72
7	7.07	20	20.00	33	32.73
8	8.08	21	20.97	34	33.74
9	9.09	22	21.94	35	34.75
10	10.10	23	22.91	36	35.76
11	11.09	24	23.88	37	36.77
12	12.08	25	24.85	38	37.78
13	13.07	26	25.82	39	38.79

There should be no greater deviation than 0.15 cc. A burette which deviates more is best not used. In the foregoing table there is a deviation of 0.30 cc. at one point.

In order to test the accuracy of a pipette, fill to the mark with distilled water at 15° C. (59° F.); empty into a previously weighed flask, weigh again and thus determine the weight of the water measured. One gram is equal to 1 cc.

Liter flasks are tested as follows:

The flask, perfectly dry and clean, is counterpoised on a balance capable of turning with .005 when carrying about 2000 grams; it is then filled to the mark with distilled water at 15° C. (59° F.) and the increase in weight should be exactly the number of grams as the cc. indicated at the mark.

When very accurate determinations are required, various factors should be taken into account, namely, atmospheric pressure, the temperature of the air, and that of the water, which should be the same. Atmospheric humidity should be of a definite degree, and the weights used should be made of specified material.

The calibration of a burette, which is graduated in mils, at 25° C., is conducted as follows:

Fill the burette to the 0 mark with distilled water at 25° C. The air should be half saturated with moisture, and of the same temperature as the water. The barometric pressure should be 760 mm. The weights used should be of brass, and the counterpoise of the flask should be of the same kind of glass as that of which the flask is made. Run out 10 mils at a time into the small counterpoised flask, and weigh each 10 mils.

Each 10 mils should weigh exactly 9.9604 gms., and every deviation found should be noted and taken into consideration in using the burette.

Example

1st 10 mils weighed 9.9610 gms. (deviation negligible)
2d 10 " " 9.8972 "
3d 10 " " 9.9543 "
4th 10 " " 10.0864 "
5th 10 " " 9.9753 "

From these data a table like the following may be constructed, and consulted whenever the burette it represents is being used.

No. of Mils as Read on Burette.	No. of Mils as Corrected.	No. of Mils as Read on Burette.	No. of Mils as Corrected.	No. of Mils as Read on Burette.	No. of Mils as Corrected.
1	1	18	17.944	35	34.983
2	2	19	18.937	36	35.995
3	3	20	19.930	37	37.008
4	4	21	20.929	38	38.020
5	5	22	21.928	39	39.033
6	6	23	22.927	40	40.046
7	7	24	23.926	41	41.046
8	8	25	24.925	42	42.046
9	9	26	25.924	43	43.046
10	10	27	26.923	44	44.046
11	10.993	28	27.922	45	45.046
12	11.986	29	28.921	46	46.046
13	12.979	30	29.920	47	47.047
14	13.972	31	30.932	48	48.047
15	14.965	32	31.945	49	49.047
16	15.958	33	32.957	50	50.047
17	16.951	34	33.970		

CHAPTER VII

METHODS OF CALCULATING RESULTS

EACH mil of a $\frac{N}{1}$ univalent volumetric solution contains $\frac{1}{1000}$ of the molecular weight in grams of its reagent, and will neutralize $\frac{1}{1000}$ of the molecular weight of a univalent substance, or $\frac{1}{2000}$ of the molecular weight of a bivalent substance.

Each mil of a $\frac{N}{1}$ bivalent volumetric solution contains $\frac{1}{2000}$ of the molecular weight in grams of its reagent, and will neutralize or combine with $\frac{1}{2000}$ of the molecular weight of a bivalent salt, or $\frac{1}{1000}$ of the molecular weight of a univalent salt.

A $\frac{N}{10}$ is only $\frac{1}{10}$ the strength of a normal solution and will neutralize only $\frac{1}{10}$ the quantity of salt, etc.

Normal and decinormal solutions of acids should neutralize normal and decinormal solutions of alkalies, volume for volume. Decinormal solution of silver nitrate and decinormal solution of hydrochloric acid or sodium chlorid should combine, volume for volume, etc.

Rules for Direct Percentage Estimations: 1. With normal solutions $\frac{1}{10}$ or $\frac{1}{20}$ (according to its atomicity) of the molecular weight in grams of the substance is weighed for titration, and the number of mils of the V.S. required to produce the desired reaction is the percentage of the substance whose molecular weight has been used.

Thus, if sodium hydroxid (NaOH) is to be examined by titration with a normal acid solution $\frac{1}{1}_0$ of its molecular weight in grams, 4 gms. is weighed out, and each mil of the acid solution required represents one per cent of the pure salt.

If sodium carbonate (Na_2CO_3) is to be titrated $\frac{1}{2}_0$ of its molecular weight in grams, 5.3 gms. is taken.

2. With decinormal solutions $\frac{1}{1}_{00}$ or $\frac{1}{2}_{00}$ of the molecular weight in grams of the substance to be analyzed is taken, and the number of mils will, in like manner, give the percentage.

The following equations will serve to explain more fully:

Sodium hydroxid with $\frac{N}{1}$ *sulphuric acid:*

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

$2 \times 40 = 80$ $\quad 2)98$

$10)40$ $\quad 49 = 1000$ mils

4.0 gms. $= 100$ mils

Sodium carbonate with $\frac{N}{1}$ *sulphuric acid:*

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

$\quad 2)98$

$20)106$ $\quad 49 = 1000$ mils

5.3 gms. $= 100$ mils

With $\frac{N}{10}$ *sulphuric acid:*

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

$2 \times 40 = 80$ $\quad 2)98$

$100)40$ $\quad 49 = 1000$ mils

0.40 gm. $= 100$ mils

In the case of a trivalent substance as citric acid $\frac{1}{3}_0$ of the molecular weight in grams is taken for analysis when a normal solution is employed and $\frac{1}{3}_{00}$ when a decinormal solution is used.

In other words, when it is desired that each mil of the

standard solution should represent one per cent of the substance upon which it acts, the rule is to take for analysis as much of the substance as is represented by 100 mils of the standard solution.

In the case of substances whose percentage of purity is high, it is advisable to take smaller quantities, in order to avoid the use of excessive quantities of standard solution. Thus sulphuric acid, which contains 92.5 per cent of absolute sulphuric acid, would require under the above conditions 92.5 mils of normal alkali solution.

In the case of this acid, if 4.9 gms. are taken for analysis, each mil of a normal alkali solution would represent one per cent of H_2SO_4.

If half of this quantity, i.e., 2.45 gms. are taken for analysis, each mil of the normal alkali will represent two per cent of H_2SO_4, and thus less of the standard solution will be required. Again, if 0.49 gm. be taken, each mil of the standard alkali will represent 10 per cent of H_2SO_4.

In the case of liquids where it is not always convenient to weigh off the exact quantity required for titration by the direct percentage method, the liquid is diluted to a convenient degree with water, and then a quantity of this diluted liquid (representing the weight required of the substance) is measured for analysis.

Example. A sulphuric acid solution of specific gravity 1.826 is to be analyzed. Two mils are accurately measured and diluted to 100 mils and then 13.41 mils of this solution (representing 0.49 gm. of the acid) are taken for analysis.

Each mil of $\frac{N}{1}$ NaOH V.S. required in the titration represents 10 per cent of absolute H_2SO_4. If $\frac{N}{10}$ NaOH V.S. is employed, each mil will represent one per cent. To de-

termine the amount of the diluted liquid to be taken we proceèd as follows:

Two mils of sulphuric acid, specific gravity 1.826, weigh 3.652 gms., therefore the 100 mils of diluted acid contain this weight, and 1 mil of the same contains 0.03652 gm.

If 0.03652 gm. are contained in 1 mil, then 0.49 gm. are contained in how many mils?

$$\begin{matrix} \text{gm.} & \text{mil} & \text{gm.} \\ .03652 & : 1 :: & 0.49 : x, \end{matrix}$$

$$x = 13.41 \text{ mils.}$$

Factors or Coefficients for Calculating the Analyses. It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed.

The best way to proceed in such a case is to find the factor.

The first step in all cases is to write the equation for the reaction which takes place between the substance under analysis and the solution used.

For instance, a solution of caustic potash is to be examined, a $\frac{N}{1}$ solution of sulphuric acid being used.

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$

$$\begin{matrix} 2)112 & 2)98 & & \\ \overline{56} & \overline{49} & = 1000 \text{ mils } \frac{N}{1} \text{ acid.} \\ 0.56 \text{ gm.} & .049 & = 1 \text{ mil } \frac{N}{1} \text{ acid.} \end{matrix}$$

The factor for KOH when $\frac{N}{1}$ solution is used is .056 gm., that being the quantity neutralized by each mil of the $\frac{N}{1}$ acid. If $\frac{N}{10}$ acid were used the factor would be .0056 gm.

The number of mils of the acid used to produce the desired result, when multiplied by the factor, gives the quantity in grams of KOH in the solution taken.

Example. If 10 grams of caustic potash solution were taken, and 40 mils of $\frac{N}{1}$ acid were required, the 10 gms. of solution contained .056 gm. $\times 40 = 2.24$ gms. of pure KOH.

To find the percentage the following formula may be used:

$$\frac{Q \times 100}{W} = \%.$$

Q = the quantity of pure substance found by calculation;
W = weight of substance taken.

If the above example is taken, we have

$$\frac{2.24 \times 100}{10} = 22.4\%.$$

Or the calculation may be made by proportion.

The quantity of the substance taken is always the first term, and the quantity of pure substance found, the second term.

The following rule is easily remembered: *As the quantity taken is to the quantity found, so is* 100 *to* x, *the percentage of pure substance in the sample.*

Three terms of the equation being given, the fourth is found by multiplying the means and dividing the product by the given extreme. By applying this rule to the above case we have

$$10 : 2.24 :: 100 : x. \qquad x = 22.4\%.$$

TABLE SHOWING THE NORMAL FACTORS, ETC., OF THE ALKALIES, ALKALI EARTHS, AND ACIDS.

Substance.	Formula.	Molecular Weight.	Normal Factor.*	Quantity of Substance to be taken† so that each mil of $\frac{N}{1}$ V.S. will indicate 1 per cent.
				Grams
Sodium hydroxid	$NaOH$	40	0.040	4.0
Sodium carbonate	Na_2CO_3	106	0.053	5.3
Sodium bicarbonate	$NaHCO_3$	84	0.084	8.4
Potassium hydroxid	KOH	56.1	0.0561	5.61
Potassium carbonate	K_2CO_3	138.2	0.0691	6.91
Potassium bicarbonate	$KHCO_3$	100.1	0.1001	10.01
Ammonia (gas)	NH_3	17.03	0.01703	1.703
Ammonium carbonate, normal	$(NH_4)_2CO_3$	96.08	0.04804	4.804
Lime	CaO	56.1	0.02805	2.805
Calcium hydroxid	$Ca(OH)_2$	74.1	0.03705	3.705
Calcium carbonate	$CaCO_3$	100.1	0.050	5.
Nitric acid	HNO_3	63.01	0.063	6.3
Hydrochloric acid	HCl	36.46	0.03646	3.646
Sulphuric acid	H_2SO_4	98.08	0.04904	4.9
Oxalic acid, crystallized	$H_2C_2O_4 \cdot 2H_2O$	126.05	0.063	6.3
Acetic acid	$HC_2H_3O_2$	60.03	0.0603	6.03

* This is the coefficient by which the number of mils of normal solution used is to be multiplied in order to obtain the quantity of pure substance present in the material examined.

† This is the quantity of substance to be taken in direct percentage estimations. Each mil of $\frac{N}{1}$ acid or alkali V.S. employed will then indicate 1 per cent; in the case of many of these substances it will, however, be better to take smaller quantities so that less of the standard solution be required. Thus if one-half the quantity be taken each mil of the $\frac{N}{1}$ V.S. will represent 2 per cent, if one-tenth of the quantity be taken each mil will represent 10 per cent. If, however, $\frac{N}{10}$ solutions be used and one-tenth of the quantity indicated in the table be taken each mil will indicate 1 per cent.

On Stating Results. In reporting the results of volumetric work, it is customary to state the quantity of pure substance found; thus in the case of salts, the quantity of the anhydrous salt is reported. It is, however, often required

to state the results according to the dualistic formulæ of Berzelius, that is, the metals are reported as oxids and the acids as anhydrids. Thus if sodium carbonate is analyzed, a statement of results by this method will give the quantity of Na_2O, spoken of as the base, soda. If we look upon sodium carbonate as Na_2OCO_2, we can readily see 106 gms. of the anhydrous salt contain 62 gms. of Na_2O.

By reference to the following equations we see that 98.08 gms. of sulphuric acid will neutralize 62 gms. of Na_2O or 106 gms. of Na_2OCO_2.

$$\underset{2)62}{Na_2O} + \underset{2)98.08}{H_2SO_4} = Na_2SO_4 + H_2O.$$

31 gms. 49.04 gms. = 1000 mils $\frac{N}{1}$ V.S.

$$Na_2OCO_2 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

$\underset{2)106}{}$

53 gms. = to 1000 mils $\frac{N}{1}$ V.S.

Thus one mil of $\frac{N}{1}$ H_2SO_4 will represent 0.031 gm. of Na_2O and 0.053 gm. of Na_2OCO_2.

In the case of sodium bicarbonate ($NaHCO_3$) two molecules contain one molecule of the base, soda, as here shown.

$$2NaHCO_3 = Na_2O,H_2O(CO_2)_2.$$

According to this 62 gms. of Na_2O represent two molecular weights (168 gms.) of $NaHCO_3$. In the case of ferrous sulphate, one molecule ($FeSO_4$) contains, according to this system, FeO and SO_3. In the same way, ferric salts contain Fe_2O_3. In stating the results of analyses of acids according to this system, the quantity of acid anhydrid found is reported, not the quantity of the whole acid. Thus if sulphuric acid is analyzed, the quantity of SO_3 is reported. In the case of phosphoric acid the quantity of P_2O_5 is stated, etc.

TABLE SHOWING THE MOLECULAR WEIGHTS AND NORMAL FACTORS FOR THE MOST COMMON OXIDS.

Name.	Formula.	Molecular Weight.*	$\frac{N}{1}$ Factor.
Soda	Na_2O	62.0	0.031 gm.
Potash	K_2O	94.2	0.0471 "
Lime	CaO	56.1	0.028 "
Magnesia	MgO	40.32	0.020 "
Lithium oxid	Li_2O	29.88	0.0149 "
Strontium oxid	SrO	103.63	0.0518 "
Barium oxid	BaO	153.37	0.0767 "
Zinc oxid	ZnO	81.37	0.0407 "
Lead oxid	PbO	223.1	0.1115 "
Arsenous oxid	As_2O_3	197.92	0.0495 "
Antimonous oxid	Sb_2O_3	288.4	0.0721 "
Mercurous oxid	Hg_2O	416.0	0.208 "
Mercuric oxid	HgO	216.0	0.108 "
Ferrous oxid	FeO	71.82	0.0718 "
Ferric oxid	Fe_2O_3	159.64	0.0798 "
Silver oxid	Ag_2O	231.76	0.1159 "
Sulphuric anhydrid	SO_3	80.07	0.040 "
Phosphoric anhydrid	P_2O_5	142.08	0.02368 "
Nitric anhydrid	N_2O_5	108.02	0.054 "
Carbonic anhydrid	CO_2	44.0	0.022 "

* Approximate.

CHAPTER VIII

ANALYSIS BY NEUTRALIZATION

This is based upon the fact that when an acid and an alkali react each loses its individuality and a neutral salt is formed, i.e., a body which has neither the character of an acid nor that of an alkali. This mutual neutralization of acid and alkali is the result of a union of the $\overset{+}{H}$· ions of the acid and the $\overset{-}{OH}$· ions of the alkali, forming non-ionized water (HOH).

An acid is a compound which in aqueous solution dissociates (ionizes) into positive and negative ions, the positive ion being H. Thus hydrochloric acid in an ionized state is $\overset{+}{H}\cdot + \overset{-}{Cl}\cdot$. Sulphuric acid ionizes into $\overset{+}{H}\cdot + \overset{+}{H}\cdot + \overset{-}{(SO_4)}$.

An alkali is a basic compound which ionizes into positive and negative ions, and in which the negative ion is (OH).

The reaction between hydrochloric acid and potassium hydroxid. in accordance with this theory, is illustrated by the following equation:

$$\overset{+}{H} + \overset{-}{Cl} + \overset{+}{K} + \overset{-}{OH} = \overset{+}{K} + \overset{-}{Cl} + HOH.$$

An acid is generally recognized as such by its color reactions with certain substances known as indicators; for example, it turns blue litmus red, and decolorizes a red phenolphthalein solution. Alkalies are recognized by their turning red litmus

blue, and by producing a deep red color with phenolphthalein.

The strength of an acid solution is ascertained by noting the quantity of alkali that is required to neutralize it. The stronger the acid, the more alkali is required. The strength of an alkali is estimated by the quantity of acid which is required to neutralize it. The estimation of the strength of acids is called **acidimetry,** while the estimation of alkalies is called **alkalimetry.**

The principal alkaline substances which may be estimated by means of standard acid solutions are the hydroxids and carbonates of sodium, potassium, lithium and ammonium, and the hydroxids and oxids of calcium, barium and strontium and the alkaloids.

When an acid is brought in contact with an alkali, a reaction takes place in which a neutral salt is formed. This is known as neutralization, and takes place between definite and invariable proportions of the reacting bodies; thus, if 112.2 parts of potassium hydroxid are mixed with 98.08 parts of absolute sulphuric acid, the alkali as well as the acid will be exactly neutralized. If only 80 parts of the acid have been added the mixture would still be alkaline, for it requires 98.08 parts of the acid to neutralize 112.2 parts of potassium hydroxid. If more than 98.08 parts of the acid have been added, the mixture would be acid, and would consist of potassium sulphate and free sulphuric acid. The reaction is thus illustrated:

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$

2K = 78.2		2H = 2.016	
2O = 32.0		S = 32.070	
2H = 2.016		4O = 64.00	
112.216		98.086	

Sodium hydroxid will unite with oxalic acid in the propor-

tion of 80.016 parts by weight of the former and 126.048 parts by weight of the latter, as the equation shows.

$$2NaOH + H_2C_2O_4 \cdot 2H_2O = Na_2C_2O_4 + 4H_2O.$$

$2Na = 46$	$6H = 6.048$
$2O = 32$	$2C = 24.000$
$2H = 2.016$	$6O = 96.000$
80.016	126.048

Ammonia water unites with hydrochloric acid as per the equation,

$$\underset{35.05}{NH_4OH} + \underset{36.46}{HCl} = NH_4Cl + H_2O.$$

Sodium carbonate with hydrochloric acid,

$$\underset{106}{Na_2CO_3} + \underset{72.92}{2HCl} = 2NaCl + H_2O + CO_2.$$

Upon a careful perusal of the foregoing equations it will be seen that since definite weights of acids neutralize definite weights of alkalies, the quantity of a certain alkali in solution can be easily determined by the quantity of an acid solution of known strength required to neutralize it, and *vice versa*.

Referring to the first equation we see that 98.086 gms. of H_2SO_4 neutralize 112.216 gms. of KOH. If we prepare a normal solution of H_2SO_4 we take half the molecular weight, 98.086 = 49.043 gms., to 1000 mils. Half the molecular weight is taken because sulphuric acid is a bivalent acid. 1000 mils of this solution will neutralize 56.108 gms. of KOH; hence 1 mil will neutralize 0.056108 gm. of KOH.

Thus if 10 gms. of a solution of KOH be treated with the above normal solution of H_2SO_4, and it is found that 25 mils of the acid solution are required to neutralize the alkali solution, the latter contains $25 \times 0.0561 = 1.40+$ gm. of pure KOH.

Since the acid and alkali as well as the neutral salt which

is formed are colorless, and no visible change takes place during the reaction, it is necessary to add some substance which by change of color will show when the neutralization is complete. Such a substance is known as an indicator.

In the case of sodium hydroxid with oxalic acid (see the second equation) we find that 126.048 gms. of crystallized oxalic acid neutralizes 80.016 gms. of NaOH. Oxalic acid, like sulphuric, is bivalent, therefore a normal solution of it contains half the molecular weight in grams, i.e., 63.024 gms. in 1000 mils.

1000 mils will neutralize 40 gms. of NaOH;
1 mil will neutralize 0.040 gm. of NaOH.

The neutralizing power of all normal acids is exactly the same, because they all contain in 1000 mils the molecular weight in grams of the acid in the case of univalent acids, and half of the molecular wieght in grams of bivalent acids.

Thus 1 mil of any normal acid will neutralize 0.0561 gm. of KOH or 0.040 gm. of NaOH or $\frac{1}{1000}$ of the molecular weight of any other univalent alkali, or $\frac{1}{2000}$ of the molecular weight of an alkali earth, the latter being bivalent. In like manner all decinormal solutions have a like neutralizing power, their neutralizing equivalence is one-tenth that of normal solutions.

Thus 1 mil of a decinormal acid will neutralize 0.00561 gm. of KOH or 0.0040 gm. of NaOH, etc.

Alkalimetry

Preparation of Standard Acid Solutions. It is possible to carry out the titration of most alkalies by means of one standard acid solution, but the same standard acid is not equally applicable in all cases; furthermore, the standard

acids are frequently employed for other volumetric operations than neutralization, and therefore it is advisable to have a variety.

The standard oxalic acid solution is preferred by some, because of the ease with which it may be prepared, provided a pure oxalic acid is to hand. It does not, however, keep very long, is unreliable for use with methyl orange, and is inapplicable for the titration of alkali earths, because it forms insoluble compounds with these metals. Standard hydrochloric acid is the most desirable for alkali earths, because it forms soluble compounds with them; its disadvantage, however, is in its volatility and its consequent uselessness in hot titrations. Standard sulphuric acid is preferred by most analysts as being the best general standard. A pure acid can be gotten without difficulty and the standard solution made from it is unaffected by boiling, and can therefore be used in hot as well as in cold titrations; it reacts sharply with the indicators and it keeps its titer indefinitely. It is, however, not suited for the titration of alkali earths, because it forms insoluble compounds with them, which precipitate and are very annoying to the operator. In the preparation of standard solutions the greatest care should be exercised in order that the product be absolutely accurate. The slightest inaccuracy in the strength of a standard solution will result in relative errors in the analysis. It is customary to prepare one standard solution, and then from this to adjust various others. For example, a normal oxalic acid may be made first, and by means of this a normal alkali solution, which in turn may be utilized for the adjusting of other standard acid solutions.

Normal Oxalic Acid V.S. ($H_2C_2O_4 \cdot 2H_2O = 126.05$, $\frac{N}{1}$ V.S. $= 63.025$ gms. in 1000 mils). Dissolve 63.025 gms. of purified

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oxalic acid * in enough distilled water to make, at or near 25° C., exactly 1000 mils.

Tenth-Normal Oxalic Acid V.S. $\left(\frac{N}{10}\right)$ V.S. = 6.3025 gms. in 1000 mils.)

Dissolve 6.3025 gms. of purified oxalic acid in sufficient distilled water to make, at or near 25° C., exactly 1000 mils of solution. Or, better: dissolve 6.45 gms. of pure crystallized oxalic acid in sufficient distilled water to measure 1000 mils. Then into a flask accurately measure 25 mils of a freshly standardized tenth-normal potassium hydroxide V.S., dilute with an equal volume of distilled water, add 3 to 5 drops of phenolphthalein T.S. and heat it to boiling. From a burette gradually add the oxalic acid solution (which is too concentrated) until the red tint of the alkali solution fails to reappear after vigorous shaking and boiling. Note the number of mils of the oxalic acid solution consumed, and then dilute it so that equal volumes of this and of the tenth-normal potassium hydroxid V.S. neutralize each other at standard temperature (25° C.). This solution deteriorates on standing, hence must be frequently renewed or restandardized.

This solution is in every respect equivalent in neutralizing power to any other tenth-normal acid V.S. with either litmus or phenolphthalein T.S. as indicator, but not with methyl orange. Its specific use in the U. S. P., however, is in standardizing or determining excess of tenth-normal potassium permanganate V.S.

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* Purified oxalic acid is in the form of colorless transparent, uneffloresced clinorhombic crystals, soluble in 10 parts of cold water, in about 3 parts of boiling water and in 2.5 parts of alcohol. Ten gms, when ignited upon platinum foil leaves not more than 0.005 gm. of residue. If more residue is left the acid should be purified by recrystallization.

Normal Hydrochloric Acid V.S. (HCl = 36.47; $\frac{N}{1}$ V.S. = 36.47 gms. in 1000 mils). Mix 110 mils of hydrochloric acid of sp.gr. 1.155 with enough water to measure, at or near 25° C., 1000 mils.

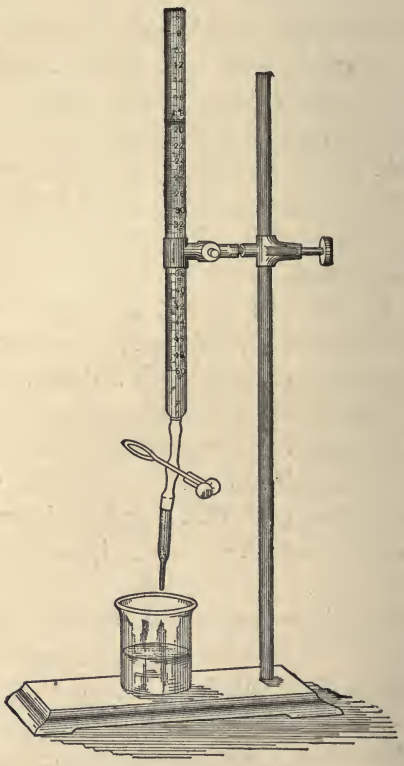

FIG. 33.

Of this liquid (which is still too concentrated) measure carefully, at 25° C., into a flask or beaker 10 mils, add 20 mils of distilled water and a few drops of methyl orange T.S., and then gradually add from a burette sufficient recently prepared and standardized $\frac{N}{1}$ potassium or sodium hydroxid

at the same temperature to just produce a permanent faint yellow tint.

Note the number of mils of $\frac{N}{1}$ alkali solution consumed and then dilute the acid solution so that equal volumes of it and $\frac{N}{1}$ alkali neutralize each other. It is usually advisable to make two or three titrations, as just described, before dilution, taking an average of the results.

Example. Assuming that the 10 mils of the acid solution required 12 mils of the $\frac{N}{1}$ alakli, each 10 mils of the acid must be diluted to 12 mils, or the whole of the remaining acid in the same proportion.

After the dilution a new trial should be made. 10 mils of the acid V.S. should required exactly 10 mils of the alkali.

This method is fairly satisfactory if an accurately standardized normal alkali hydroxid solution is at hand; the latter, however, always contains a small qunatity of carbonate, hence methyl orange is most desirable as an indicator.

Standardization by Means of Sodium Carbonate. Pure anhydrous sodium carbonate may be obtained by heating to dull redness a few grams of *pure* sodium bicarbonate for about thirty minutes. The resulting carbonate is practically free from impurity.

The sodium bicarbonate loses on ignition one-half of its carbonic acid gas:

$$2NaHCO_3 + Heat = Na_2CO_3 + CO_2 + H_2O.$$

The bicarbonate should, however, be tested before igniting, and if more than traces of chlorid, sulphate, or thiosulphate, are found, these may be removed by washing a few hundred grams, first with a saturated solution of sodium bicarbonate, and afterward with distilled water.

0.53 gm. of the pure anhydrous sodium carbonate is accurately weighed and dissolved in about 200 mils of distilled water in a flask and a few drops of methyl orange T.S. added as indicator. The acid to be "set" of "standardized" is then run into the sodium carbonate solution until a permanent light-red color is produced. It should require exactly 10 mils of the $\frac{N}{1}$ acid solution.

If 8 mils of the acid solution are consumed to bring about the required result, then every 8 mils must be diluted to 10 mils, or the whole of the remaining solution must be diluted in this proportion:

$$\underset{\substack{2)106\\ 53\text{ gms.}\\ 0.53\text{ gm.}}}{Na_2CO_3} + \underset{\substack{2)72.9\\ 36.45}}{2HCl} = 2NaCl + H_2O + CO_2.$$

$$= 1000 \text{ mils } \frac{N}{1} \text{ V.S.}$$

$$= 10 \text{ mils } \frac{N}{1}$$

Instead of attempting to weigh *exactly* 0.53 gm. of the anhydrous sodium carbonate, it is better to take a larger quantity (about 2 gms.) weighed accurately. Dissolve this in 100 mils of distilled water, add 2 or 3 drops of methyl orange T.S. and run into it, little by little, from a burette the acid solution to be standardized, reducing the flow to drops toward the end until a pink color is obtained. Make 2 or 3 trials, and take the average number of mils consumed.

One gm. of pure anhydrous sodium carbonate requires for exact neutralization 18.868 mils of normal acid V.S.

Assuming that 2.3 gms. of the anhydrous carbonate were taken, and this required 38.2 mils of the trial acid. Then

$$2.3 \times 18.868 = 43.3964 \text{ mils.}$$

$$43.3964 : 38.2 :: 100 : x. \quad x = 88.26.$$

Now adjust the acid by measuring 882.6 mils and diluting with distilled water to make 1000 mils.

This method may be employed as well for the standardization of sulphuric or oxalic acid.

Other Methods for standardizing hydrochloric acid V.S. are: (*a*) by means of silver nitrate (gravimetrically and volumetrically); (*b*) by means of borax; (*c*) by means of the specific gravity; (*d*) by means of calc-spar.

Normal Sulphuric Acid V.S. ($H_2SO_4 = 98.09$; $\frac{N}{1}$ V.S. = 49.045 gms. in 1000 mils). Mix carefully 30 mils of pure concentrated sulphuric acid (sp.gr. 1.835) with enough water to make about 1050 mils, and allow the liquid to cool to about 25° C.

Titrate 10 mils of this liquid in the manner described under $\frac{N}{1}$ hydrochloric acid, and dilute it so that equal volumes of the acid and the alkali will neutralize each other.

The standardization of the normal sulphuric acid solution may also be effected by the use of pure anhydrous sodium carbonate, as described under normal hydrochloric acid V.S., and by various other methods, among which are: (*a*) the iodometric; (*b*) the specific gravity method; (*c*) the borax method; (*d*) by precipitation with barium chlorid (gravimetrically).

Standard acid solutions are used in other strengths besides normal, namely, *Half-normal* $\frac{N}{2}$, *Fifth-normal* $\frac{N}{5}$, *Tenth-normal* $\frac{N}{10}$, *Twentieth-normal* $\frac{N}{20}$, *Fiftieth-normal* $\frac{N}{50}$, and *Hundredth-normal* $\frac{N}{100}$.

Estimation of Alkali Hydroxids

Potassium and sodium hydroxids are usually titrated with $\frac{N}{1}$ sulphuric or hydrochloric acid; they are, however, so prone to absorb carbon dioxid out of the air that they are seldom free from carbonate, and hence the selection of an indicator

is a matter of some importance. Phenolphthalein or litmus may be employed, but it is then advisable to boil the solution while titrating, in order to drive off the liberated carbon dioxid, because the latter gives an acid reaction with phenolphthalein and litmus and thus causes an end-reaction tint to appear before neutralization is complete. It is better, usually, to employ an indicator which is not affected by carbon dioxid. Methyl orange is mostly preferred; cochineal and Congo red are also useful. These indicators are especially serviceable in the presence of carbonates in that they are not affected by carbon dioxid, and can therefore be employed in direct titrations without the use of heat.

The quantity of carbonate in a recent sample of sodium or potassium hydroxid is so small usually that it is customary to disregard it and to report the total alkalinity as hydroxid.

A definite quantity of the sample (from 0.5 gm. to 1 gm. of the solid or an equivalent of a solution) is taken for analysis, dissolved in 30 to 50 mils of water in a white porcelain dish or a beaker placed over a white surface, and a few drops of a suitable indicator added.

The vessel is then placed beneath a burette containing the standard acid solution and the latter run in, drop by drop, until the last drop just causes the color to change. The solution should be rotated or stirred after each addition of the standard acid.

The alkali hydroxids are so exceedingly hygroscopic that they take up water from the air while being weighed; it is therefore difficult to make a direct weighing with any degree of accuracy.

The best way is to take a small piece of the sample (about 1 gm.), place it immediately in a tared stoppered flask and take the weight accurately. It is then dissolved in water, transferred to the porcelain dish or beaker and titrated.

Potassium Hydroxid (KOH = 56.1). An accurately weighed portion (preferably less than 1 gm.), is placed in a small beaker, dissolved in 50 mils of water, three drops of methyl orange added, and the titration begun with $\frac{N}{1}$ sulphuric acid and continued until the yellow color of the solution is changed to pale red. Then the burette is carefully read to see how much of the acid solution was used. The number of mils of the latter are multiplied by the normal factor for KOH (0.0561) and the result is the quantity of pure KOH in the sample taken for analysis.

The following equation illustrates the reaction:

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$

$2)112.2$ $\quad$ $2)98.09$

56.1 gms. $\quad$ 49.045 gms., quantity in 1000 mils of $\frac{N}{1}$ acid V.S.

0.0561 gm. (the factor for KOH), quantity neutralized by 1 mil of $\frac{N}{1}$ acid.

Thus 1000 mils of $\frac{N}{1}$ H_2SO_4 V.S. containing 49.045 gms. of absolute H_2SO_4 will neutralize 56.1 gms. of KOH. Therefore each mil of $\frac{N}{1}$ H_2SO_4 V.S. will neutralize 0.0561 gm. of pure KOH.

Example. In the above analysis let it be assumed that 0.915 gm. of potassium hydroxid were taken and that 15.3 mils of the standard acid were required to neutralize it, then 0.0561 gm. $\times$ 15.3 = 0.8583 gm., the quantity of pure KOH in the 0.915 gm. taken.

The percentage is then calculated in this way:

$$0.915 : 0.8583 :: 100 : x; \qquad x = 93.8 + \text{per cent.}$$

$$\frac{0.8583 \times 100}{0.915} = 93.8.$$

The fixed alakli hydroxids are rarely free from carbonate, through absorption of carbon dioxid from the air.

In the foregoing method, the carbonate is calculated as hydroxid, hence the assay is fallacious. The method of the U. S. P. IX separates the carbonate by precipitating with barium chlorid, filtering, and titrating the filtrate with normal hydrochloric acid V.S., using phenolphthalein as indicator. The use of standard sulphuric acid V.S. is inadmissible in this method because it reacts with barium chlorid, producing a precipitate of barium sulphate.

The U. S. P. Method is as follows:

Take about 10. gms. of potassium hydroxid, accurately weighed in a glass-stoppered weighing bottle, dissolve in 250 mils of distilled water, which has been previously boiled and cooled (to expel carbon dioxid), add 30 mils of barium chlorid T.S. and then dilute with distilled water to 500 mils. Thoroughly agitate the liquid and filter it through a dry filter into a dry flask. Reject the first 20 mils, and titrate 200 mils of the clear filtrate with normal hydrochloric acid V.S., using phenolphthalein T.S. as indicator.

Sodium Hydroxid ($NaOH=40$). This is estimated in exactly the same manner as described for potassium hydroxid, the following equation being applied:

$$\underset{\substack{2)80\\ 40\text{ gms.}}}{2NaOH} + \underset{\substack{2)98.09\\ 49.045\text{ gms.}}}{H_2SO_4} = Na_2SO_4 + 2H_2O.$$

$$= 1000\text{ mils } \frac{N}{1}\text{ V.S.}$$

$$.040\text{ gm.} \qquad 1\text{ mil } \frac{N}{1}\text{ V.S.}$$

The factor.

The official solutions of potassium and of sodium hydroxid are estimated in this same manner, 10 mils may be taken for analysis, diluted with 20 mils of water.

Ammonia Water ($NH_3 \cdot H_2O$). Three mils of ammonia water are put into a stoppered weighing bottle and the weight

taken. Forty mils of water are then added and the solution titrated with $\frac{N}{1}$ sulphuric acid. As indicator, litmus, methyl orange or rosolic acid may be used. Phenolphthalein is useless for titrating ammonia, and even methyl orange and rosolic acid are unsuitable in the presence of much salts of ammonium. Because of the volatile character of ammonia its solutions readily lose strength upon exposure. It is therefore best to measure a quantity into a weighing bottle and find its weight as directed for potassium hydroxid. If the specific gravity of the ammonia solution is known, the weight of a given volume is easily calculated, it being only necessary to multiply the volume in mils by the sp.gr. Thus, if the sp.gr. of an ammonia solution is 0.9585 and the volume taken is 3 mils, the weight of the 3 mils is $3 \times 0.9585 = 2.8755$ gms.

In the titration with $\frac{N}{1}$ sulphuric acid each mil of the latter represents 0.017 gm. of NH_3, as shown by the equation

$$2NH_3 \cdot H_2O + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O.$$

$$\underset{17 \text{ gms.}}{\underline{2)34}} \qquad \underset{49.045 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}{\underline{2)98.09}}$$

$$\underset{\text{Factor.}}{.017} = 1 \text{ mil } \frac{N}{1} \text{ V.S.}$$

If 16.9 mils of $\frac{N}{1}$ acid were required in the above assay, then 0.017 gm. $\times$ 16.9 = 0.2873 gm., the quantity of pure NH_3 in the 3 mils (2.8755 gms.) of ammonia water taken.

The percentage is found as follows:

If 3 mils of ammonia water weighing 2.8755 gms. contain 0.2873 gm. of NH_3, 100 gms. of ammonia water will contain $\times$ gm. of NH_3,

$$\frac{0.2873 \times 100}{2.8755} = 9.99 \text{ per cent.}$$

Stronger ammonia water and spirit of ammonia may be estimated in the same manner.

Estimation of Alkali Carbonates

When carbonates are treated with acids carbonic-acid gas is liberated. This gas shows an acid reaction with most indicators, and the reaction will seem to be completed before the alkali is entirely neutralized.

To avoid this, the titration may be conducted at the boiling temperature (*hot way*) in order to drive off the carbon dioxid. The standard acid being added until two minutes' boiling fails to restore the color indicating alkalinity. If the titration is conducted at a boiling temperature, it is advisable to attach to the lower end of the burette a long rubber tube with a pinch-cock fixed about midway on the tube.

The boiling can then be done at a little distance from the burette and the expansion of the standard solution therein thus prevented.

Another method is to add to the carbonate a measured excess of the standard acid, and then after boiling to drive off the carbon dioxid, an indicator is added, and the excess of standard acid determined by titration with a standard alkali (*residual titration way*). The quantity of the latter, deducted from the quantity of the standard acid taken, gives the quantity of the latter which reacted with the carbonate. Still another method is to titrate the carbonate direct, without heat (*cold way*), using an indicator which is not affected by carbon dioxid. The best of the indicators which are not so affected is methyl orange; others are cochineal and Congo red. When employing methyl orange as an indicator standard oxalic acid solution should not be used, as the end-reaction is very indefinite and unreliable.

The end-reaction with this indicator is at all events not a clearly marked one, and considerable practice and an eye for color is required to detect the point at which yellow changes to

pale pink. It is a good plan to have on the bench two vials, one containing an acid and the other an alkali tinted with methyl orange, with which comparisons can be made.

FIG. 34

Potassium Carbonate ($K_2CO_3 = 138.2$). Weigh carefully one gram of the salt, previously dried to constant weight at 180° C. Dissolve in 25 mils of distilled water in a beaker or flask, add a few drops of methyl orange T.S., and titrate with normal sulphuric acid until a faint orange-red color appears.

$$\underset{\frac{2)138.2}{69.1 \text{ gms.}}}{K_2CO_3} + \underset{\frac{2)98.09}{49.045 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}}{H_2SO_4} = K_2SO_4 + H_2O + CO_2.$$

Each mil of $\frac{N}{1}$ H_2SO_4, therefore, represents 0.0691 gm. of pure potassium carbonate.

If 14.3 mils of the normal acid are required the salt contains

14.3×0.0691 gm.=0.98813 gm. of pure K_2CO_3 or 98.813 per cent. If it is desired to use litmus or phenolphthalein, it will be necessary to boil the solution as described above.

Other alkali carbonates are estimated in exactly the same manner as described for potassium carbonate.

Potassium Bicarbonate ($KHCO_3=100.1$).

$$\underset{\substack{2)200.2\\ 100.1\text{ gms.}}}{2KHCO_3} + \underset{\substack{2)98.09\\ 49.045\text{ gms.}=1000\text{ mils }\frac{N}{1}\text{ V.S.}}}{H_2SO_4} = K_2SO_4 + 2H_2O + CO_2.$$

Each mil of $\frac{N}{1}$ acid V.S.=0.1001 gm. of $KHCO_3$.

Previous to weighing, this salt should be dried to constant weight in a desiccator over sulphuric acid.

Sodium Carbonate (crystallized) ($Na_2CO_3 \cdot 10H_2O=286.16$).

$$\underset{\substack{2)286.16\\ 143.08\text{ gms.}}}{Na_2CO_3.10H_2O} + \underset{\substack{2)98.09\\ 49.045\text{ gms.}=1000\text{ mils }\frac{N}{1}\text{ V.S.}}}{H_2SO_4} = Na_2SO_4 + 11H_2O + CO_2.$$

Each mil of $\frac{N}{1}$ acid=0.143 gm. crystallized sodium carbonate.

Sodium Carbonate (anhydrous) ($Na_2CO_3=106$).

$$\underset{\substack{2)106\\ 53\text{ gms.}}}{Na_2CO_3} + \underset{\substack{2)98.09\\ 49\,045\text{ gms.}=1000\text{ mils }\frac{N}{1}\text{ V.S.}}}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2.$$

Each mil of $\frac{N}{1}$ acid=0.053 gm. Na_2CO_3.

Sodium Bicarbonate ($NaHCO_3=84$).

$$\underset{\substack{2)168\\ 84\text{ gms.}}}{2NaHCO_3} + \underset{\substack{2)98.09\\ 49.045\text{ gms.}=1000\text{ mils }\frac{N}{1}\text{ V.S.}}}{H_2SO_4} = Na_2SO_4 + 2H_2O + 2CO_2.$$

Each mil of $\frac{N}{1}$ acid=0.084 gm. $NaHCO_3$.

Previous to weighing, the salt should be dried to constant weight in a desiccator over sulphuric acid.

Lithium Carbonate ($Li_2CO_3 = 73.88$).

$$Li_2CO_3 + H_2SO_4 = Li_2SO_4 + H_2O + CO_2.$$

$2)73.88$ $\quad$ $2)98.09$

36.94 gms. $\quad$ 49.045 gms. $= 1000$ mils $\frac{N}{1}$ V.S.

Each mil of $\frac{N}{1}$ acid $= 0.03694$ gm. Li_2CO_3.

The U.S.P. IX recommends residual titration for this salt. Previous to weighing it should be dried to constant weight at 100° C. 1.5 gm. is dissolved in 50 mils of normal sulphuric acid V.S. and the solution titrated with normal potassium hydroxid V.S., using methyl orange T.S. as indicator.

Ammonium Carbonate ($N_3H_{11}C_2O_5 = 157.03$). Normal ammonium carbonate has the formula $(NH_4)_2CO_3$, but the normal salt loses upon exposure NH_3 and H_2O. The commercial salt, therefore, generally is a mixture of bicarbonate and carbamate.

$$(NH_4)_2CO_3 - NH_3 = NH_4HCO_3;$$
$$(NH_4)_2CO_3 - H_2O = NH_4NH_2CO_2.$$

The commercial carbonate is therefore generally expressed thus:

$$NH_4HCO_3 . NH_4NH_2CO_2 \quad \text{or} \quad N_3H_{11}C_2O_5.$$

This salt may be estimated by direct titration with normal or decinormal acid, using rosolic acid or methyl orange as an indicator.

Two grams of the salt are taken, dissolved in about 50 mils of water and titrated with $\frac{N}{1}$ H_2SO_4 V.S. The reaction is as follows:

$$2N_3H_{11}C_2O_5 + 3H_2SO_4 = 3(NH_4)_2SO_4 + 4CO_2 + 2H_2O.$$

$6)314.06$ $\quad$ $6)294.18$

52.34 gms. $\quad$ 49.045 gms. $= 1000$ mils $\frac{N}{1}$ acid V.S.

Each mil of $\frac{N}{1}$ acid V.S. represents 0.052 gm. of $N_3H_{11}C_2O_5$ or 0.017 gm. of NH_3. The U.S.P. salt should contain between 30 and 32 per cent of NH_3.

If in this titration 37.3 mils of the standard acid are required then the two grams of ammonium carbonate contained 0.052 gm. $\times 37.3 = 1.939$ gms. of the salt.

$$\frac{1.939 \times 100}{2} = 96.95 \text{ per cent.}$$

If rosolic acid is used as indicator heat must be applied to expel carbon dioxid. The estimation of the carbonic acid may be effected by precipitating a definite weight of the salt with barium chlorid, collecting the precipitated barium carbonate, dissolving it in a measured excess of normal hydrochloric acid and retitrating with normal alkali.

The method usually employed by skilled analysts (*the residual titration method*), is to add a measured excess of the standard acid solution, and thus convert the ammonium carbonate into the less volatile ammonium sulphate; then gently boil to get rid of CO_2, and titrate back with a standard alkali V.S. (using methyl orange as an indicator) until the excess of acid is neutralized. The quantity of free acid thus found, when deducted from the amount of acid first added, gives the quantity which was required to neutralize the ammonium carbonate.

Thus 2 gms. (in solution) of ammonium carbonate are treated with 50 mils of $\frac{N}{1}$ H_2SO_4 V.S., which is more than sufficient to neutralize it; the solution is then gently boiled to drive off CO_2, a few drops of litmus tincture added, and then titrated with $\frac{N}{1}$ KOH V.S. until the litmus no longer shows an acid reaction and the solution is neutral. If methyl orange is used as an indicator here, boiling is not necessary.

Let us assume that 12.7 mils of the $\frac{N}{1}$ KOH V.S. were used. By deducting the 12.7 mils from the 50 mils of $\frac{N}{1}$ acid first added, we find 37.3 mils of the acid went into combination with the ammonium salt, the calculation is then made as described above.

Mixed Alkali Hydroxid and Carbonate

If it is desired to ascertain the proportion in which these exist in a mixture, we proceed as follows:

First determine the total alkalinity by means of normal hydrochloric acid, using methyl orange as an indicator. Then dissolve a like quantity of the mixture in 150 mils of water and add sufficient barium chlorid to precipitate all of the carbonate as barium carbonate, and then add water to make 200 mils and set aside to settle. When the supernatant liquid is clear take one-fourth (50 mils) of it, and titrate with normal hydrochloric acid, using phenolphthalein as indicator.* The number of mils multiplied by 4 will be the quantity of normal acid required by the caustic alkali. The difference between this and the number of mils representing the total alkalinity is calculated as carbonate.

Example. Assuming that we are analyzing a mixture of sodium hydroxid and carbonate.

Two grams of the substance are dissolved in water and titrated with normal acid solution. 43.2 mils of the latter are required. Another 2 gms. is dissolved, treated with barium chlorid as directed, and one-fourth of the clear solution titrated

* The slight error which occurs in this method because the volume of the precipitate is included in the measured liquid, may be overcome by using the entire quantity of liquid, including the precipitate (instead of taking one-fourth of it), and titrating with oxalic acid V.S. in the presence of phenolphthalein. Oxalic acid in very dilute solutions does not react with alkali earth carbonates.

with normal acid. 5.6 mils are required; then $5.6 \times 4 = 22.4$ mils, representing the sodium hydroxid.

43.2 mils = total alkalinity;
$-22.4 \times 0.040 = 0.896$ gm. sodium hydroxid.

$20.8 \times 0.053 = 1.1024$ gms. sodium carbonate.

Another way is to filter the mixture after barium chlorid has been added, titrate the filtrate with normal acid to find the quantity of hydroxid, then dissolve the precipitated barium carbonate in normal hydrochloric acid in excess, and retitrate with normal alkali, thus ascertaining the amount of carbonate.

When the alkaline carbonate is present in very small quantities the method of Lunge may be employed.

A few drops of phenacetolin solution are added to impart a scarcely perceptible yellow to the liquid. Normal acid solution is then run in until a pale rose tint appears, indicating that all the alkali hydroxid is neutralized; the volume of acid is noted, and the titration continued; the red color is intensified, and when the carbonate is entirely decomposed a golden-yellow color results.

Considerable practice is required with solutions of known composition to accustom the eye to the changes of color.

Mixed Alkali Bicarbonates and Carbonates

Thompson's Method. Take 2 grams of the salt and dissolve in 100 mils of water. Divide the solution into two equal parts and titrate one portion with normal acid solution, using methyl orange as indicator, and note the quantity required. We will assume 13 mils.

Then treat the second portion with a measured excess (say 25 mils) of normal sodium hydroxid solution free from

CO_2. This converts the bicarbonate into carbonate. Now add an excess of pure neutral barium chlorid solution in order to precipitate all the carbonate as barium carbonate, and then titrate with normal acid, using phenolphthalein as indicator, to determine the excess of sodium hydroxid. 15 mils are required. Thus

$25 - 15 = 10$ mils, the equivalent of bicarbonate;
and $13 - 10 = 3$ mils, the equivalent of carbonate;
$10 \times .084 = .840$ gm. sodium bicarbonate;
$3 \times .053 = .159$ gm. sodium carbonate.

Sodium Borate (Borax) ($Na_2B_4O_7 + 10H_2O = 382.16$). Dissolve 5 gms. of the salt in 100 mils of distilled water and titrate the solution with normal hydrochloric acid V.S., using methyl orange T.S. as indicator.

$$\underset{382.16}{Na_2B_4O_7 \cdot 10H_2O} + 2HCl = 2NaCl + 4H_3BO_3 + 5H_2O.$$

Each mil of normal HCl V.S. corresponds to 0.19108 gm. of crystallized borax or to 0.101 gm. of anhydrous borax.

Sodium Cacodylate ($Na(CH_3)_2AsO_2 = 160.01$). This salt is assayed by titration with normal HCl V.S. in the presence of methyl orange. Each mil of the acid V.S. corresponds to 0.160 gm. of the salt.

This salt is occasionally slightly acid in reaction; if so, it should be carefully neutralized to phenolphthalein before titration is begun.

Sodium Glycerophosphate ($Na_2C_3H_5(OH)_2PO_4 = 216.1$). This salt is titrated with half-normal hydrochloric acid V.S. in presence of methyl orange.

Each mil of $\frac{N}{2}$ acid V.S. corresponds to 0.10805 gm. oi the salt.

Estimation of Organic Salts of the Alkalies

The tartrates, citrates and acetates of the alkali metals are converted by ignition into carbonates, the whole of the base remaining in the form of carbonate.

Each molecular weight of a normal tartrate gives when ignited one molecular weight of carbonate:

$$\underline{K_2}C_4H_4O_6 = \underline{K_2}CO_3.$$

Every two molecular weights of an acetate or an acid tartrate give one molecular weight of carbonate:

$$\underline{2K}C_2H_3O_2 = \underline{K_2}CO_3;$$
$$\underline{2K}HC_4H_4O_6 = \underline{K_2}CO_3.$$

Every two molecular weights of a normal citrate give three molecular weights of carbonate:

$$\underline{2K_3}C_6H_5O_7 = \underline{3K_2}CO_3.$$

These reactions are taken advantage of in volumetric analysis, and the tartrates, citrates and acetates of the alkalies are indirectly estimated by calculating upon the quantity of carbonate formed by burning them, the quantity of carbonate being found by titration in the usual manner.

The Process. Before igniting, the salt to be examined should be thoroughly dried in a desiccator over calcium chlorid or in a drying oven, the latter only for such salts as have no water of crystallization in their composition. If the weight is taken before and after, the amount of moisture present is determined. One or two grams of the dried salt is weighed accurately, placed in a porcelain crucible, and heat applied gradually, until dull redness is reached and white fumes cease to be given off. Upon applying heat to the salt, the latter swells, fuses, and then boils, and if the heat is applied too rapidly at this point, there is apt to be a considerable loss

of material through sputtering. The flame of the burner must not come in contact with the carbonized mass. The completion of the ignition is known to be reached when the black contents of the crucible is dry and crisp. The crucible is then allowed to cool, its contents disintegrated with the aid of a stout glass rod and then treated with boiling water to dissolve out the alkali carbonate, and the solution filtered through a small, wetted filter into a flask or beaker. The filtrate should be perfectly colorless. If it has a yellow or brownish color it indicates incomplete ignition and should be rejected, and a fresh quantity of the salt subjected to ignition. The contents of the crucible and the filter should be washed with several small portions of water until the washings no longer show an alkaline reaction. The filtrate mixed with the wash water is now titrated with standard sulphuric or hydrochloric acid, using methyl orange as the indicator. From the quantity of carbonate found in the filtrate, the equivalent amount of the organic salt may be calculated. The quantity of standard acid employed is multiplied direct by the factor for the original salt. The residual titration method, using an excess of half-normal sulphuric acid V.S., boiling, and retitrating with half-normal potassium hydroxid V.S., is recommended in the U.S.P.

In the case of organic salts of the alkali earths,* residual titration should always be resorted to. The residue in the crucible being dissolved in standard hydrochloric acid, and retitrated with standard alkali.

Lithium salts, because of the sparing solubility of the carbonate in water, should also be titrated by the residual method.

Potassium Tartrate ($K_2C_4H_4O_6 = 226.23$). Two grams of

* Organic salts of the alkali earths subjected to ignition as above are reduced partly to oxids.

the salt is placed in a platinum or porcelain crucible and heated to redness in contact with the air until completely charred; that is to say, until nothing is left in the crucible but carbonate and free carbon.

The crucible is now cooled, and its contents treated with boiling water, which dissolves the potassium carbonate, the carbon being separated by filtration. In order to obtain every trace of carbonate it is well to wash the crucible with several small portions of hot water, and add the washings to the rest of the filtrate through the filter.

If the salt is completely carbonized the filtrate will be colorless, but if the carbonization is not complete the solution will be more or less colored and should be rejected, and a fresh quantity of the salt subjected to ignition.

To the filtrate, which contains potassium carbonate, add a few drops of methyl orange, and titrate with $\frac{N}{1}$ sulphuric acid V.S. until a light orange-red color appears and the carbonate is neutralized.

The following equations will explain the reactions:

$$\underset{226.2}{K_2C_4H_4O_6} = \underset{138.2}{K_2CO_3} + C_2 + CO + 2H_2O$$

then

$$\underset{138.2}{K_2CO_3} + \underset{98.07}{H_2SO_4} = K_2SO_4 + H_2O + CO_2$$

therefore

$$\underset{2)226.2}{K_2C_4H_4O_6} = \underset{2)138.2}{K_2CO_3} = \underset{2)98.07}{H_2SO_4}$$

$$113.1 \text{ gms.} = 69.1 \text{ gms.} = 49.03 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}$$

and each mil of $\frac{N}{1}$ H_2SO_4 represents 0.1131 gm. of potassium tartrate.

Example. Two grams of potassium treated as described

above require 16.3 mils of $\frac{N}{1}$ H_2SO_4. It therefore contains $0.1131 \times 16.3 = 1.8435$ gms.

$$\frac{1.8435 \times 100}{2} = 92.17 \text{ per cent.}$$

Potassium and Sodium Tartrate ($KNaC_4H_4O_6.4H_2O = 282.22$) (*Rochelle Salt*). This salt is treated in exactly the same way as described for potassium tartrate.

When ignited the double tartrate is converted into a double carbonate of potassium and sodium:

$$\underset{210.1}{KNaC_4H_4O_6} = \underset{122.1}{KNaCO_3} + \text{etc.};$$

then

$$KNaCO_3 + H_2SO_4 = KNaSO_4 + CO_2 + H_2O$$

therefore

$$\underset{\frac{2)210.1}{105.05}}{KNaC_4H_4O_6} = \underset{\frac{2)122.1}{61.05}}{KNaCO_3} = \underset{\frac{2)98.07}{49.03 = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}}{H_2SO_4}$$

and each mil of $\frac{N}{1}$ H_2SO_4 represents 0.10505 gm. of $KNaC_4H_4O_6$.

Example. If one gram of rochelle salt treated as above described requires 7 mils of $\frac{N}{1}$ sulphuric acid, it contains $0.10505 \times 7 = 0.7353$ gm. $= 73.53$ per cent.

According to the U.S.P. IX this salt is assayed by residual titration, using half-normal sulphuric acid V.S., as follows:

Heat two gms. of the salt in a porcelain crucible, until thoroughly carbonized. Allow the carbonized mass to cool, disintegrate it with the aid of a stout glass rod and transfer the mass and crucible to a beaker. Add 50 mils of distilled water and 50 mils of half-normal sulphuric acid V.S., cover the beaker

with a watch glass and boil the contents for thirty minutes. Then filter the solution and wash the residue with hot distilled water until the washings cease to redden blue litmus paper. Now determine the residual acid in the cooled filtrate by titration with half-normal KOH V.S., using methyl orange as indicator.

Subtract the number of mils of half-normal alkali V.S. used from 50 mils (the quantity of half-normal acid V.S. taken). The remainder represents the quantity of half-normal sulphuric acid V.S. which reacted with the carbonate in the charred mass. This, multiplied by $\frac{N}{2}$ factor for rochelle salt, represents the weight of the latter in the amount taken for analysis. The foregoing equations show the normal factor for anhydrous rochelle salt to be 0.10505 gm., hence the half normal factor for the same is 0.05253 gm.

Hence, if in the above assay 22 mils of half-normal KOH V.S. were used, this quantity deducted from 50 mils, leaves 28 mils, the quantity of half-normal sulphuric acid which was taken up by the alkaline carbonized mass; then $0.05253 \times 28 = 1.470$ gm. of $KNaC_4H_4O_6$ in the 2 gms. of rochelle salt taken for analysis $= 73.5$ per cent.

Potassium Bitartrate ($KHC_4H_4O_6 = 188.1$) (*Cream of Tartar*). The estimation of this salt is affected in the same way as the tartrate.

The bitartrate having but one atom of potassium in its molecule, it takes two molecules to form one molecule of carbonate.

$$\underset{\substack{2)376.2\\ 188.1 \text{ gms.}}}{2KHC_4H_4O_6} = K_2CO_3 + \underset{\substack{2)98.07\\ 49.03 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}}{H_2SO_4}$$

Each mil of $\frac{N}{1}$ H_2SO_4 V.S. $= 0.1881$ gm. of $KHC_4H_4O_6$.

Another way of estimating bitartrate is to dissolve a weighed quantity of hot water and titrate with $\frac{N}{1}$ potassium hydroxid until neutral, and thus the amount of tartaric acid existing as bitartrate is found. The bitartrate is acid in reaction. In detail the method is as follows:

Two grams of the bitartrate are dissolved in 100 mils of hot water, a few drops of phenolphthalein T.S. added, and then titrated with $\frac{N}{1}$ KOH V.S. until a faint pink color indicates that all of the acid has been neutralized. Not less than 10.6 mils of the normal alakli should be required, corresponding to 99.6 per cent of pure salt.

The following equation will show the reaction:

$$\underset{188.1}{KHC_4H_4O_6} + \underset{56.1}{KOH} = K_2C_4H_4O_6 + H_2O.$$

$= 1000$ mils of $\frac{N}{1}$ KOH V.S.

Each mil of $\frac{N}{1}$ KOH V.S. represents 0.1881 gm. of $KHC_4H_4O_6$.

If 10.6 mils are required for neutralization, then $10.6 \times 0.1881 = 1.993+$ gms.:

$$\frac{1.993 \times 100}{2} = 99.6 \text{ per cent.}$$

Potassium Citrate ($K_3C_6H_5O_7 = 306.3$).

$$\underset{6)612.6}{2K_3C_6H_5O_7} = \underset{6)414.6}{3K_2CO_3} = \underset{6)294.18}{3H_2SO_4}.$$

102.1 gms. $= 69.1 =$ 49.03 gms. $= 1000$ mils $\frac{N}{1}$ acid.

Thus each mil of $\frac{N}{1}$ acid represents 0.1021 gm. of pure potassium citrate, and each mil of $\frac{N}{2}$ acid represents 0.0510 gm.

Potassium Acetate ($KC_2H_3O_2 = 98.1$). In estimating potassium acetate the salt is ignited and the residue treated in

exactly the same manner as in the estimation of the citrates and tartrates before mentioned.

$$2KC_2H_3O_2 = K_2CO_3.$$
$$\underset{98.1 \text{ gms.}}{\overset{2)196.2}{}} = 1000 \text{ mils } \frac{N}{1} H_2SO_4.$$

Each mil therefore of $\frac{N}{1}$ H_2SO_4 corresponds to 0.0981 gm. of potassium acetate.

Sodium Acetate ($NaC_2H_3O_2.3H_2O = 136.09$).

$$2(NaC_2H_3O_2.3H_2O) = Na_2CO_3,$$

Each mil of $\frac{N}{2}$ H_2SO_4 V.S. represents 0.06804 gm. of crystallized sodium acetate.

Sodium Benzoate ($NaC_7H_5O_2 = 144.05$).

$$2NaC_7H_5O_2 = Na_2CO_3.$$

Each mil of $\frac{N}{2}$ H_2SO_4 V.S. represents 0.07202 gm. of sodium benzoate.

Sodium Salicylate ($NaC_7H_5O_3 = 160.05$).

$$2NaC_7H_5O_3 = Na_2CO_3.$$

Each mil of $\frac{N}{2}$ H_2SO_4 V.S. represents 0.08002 gm. of sodium salicylate.

Lithium Citrate ($Li_3C_6H_5O_7 = 209.92$). As stated before, the organic salts of lithium and those of the alkali earth metals are best titrated by the residual method, after ignition, because the carbonates formed are insoluble in water. It is likewise best to use standard hydrochloric instead of standard sulphuric acid. The process for lithium citrate here given exemplifies the method.

Two grams of the salt is thoroughly ignited in a porcelain crucible as described for potassium tartrate. The residue of lithium carbonate is then dissolved out of the crucible by add-

ing 50 mils of $\frac{N}{2}$ hydrochloric V.S. and filtering. The crucible and filter are washed with several small quantities of water and the washings added to the acid filtrate. Three drops of methyl orange are now added, and the solution titrated with $\frac{N}{2}$ potassium hydroxid V.S. until the yellow color appears. Assuming that 8 mils of the standard alkali were required, then 50−8=42 mils, the quantity of half-normal hydrochloric acid which reacted with the lithium carbonate. This quantity multiplied by the half-normal factor for lithium citrate, 0.03498, gives the weight of pure salt in the 2 gms. taken.

$$0.03498 \times 42 = 1.4731 + \text{ gm. or } 73.65 \text{ per cent.}$$

Calcium Lactate ($Ca(C_3H_5O_3)_2 + 5H_2O = 308.23$). This is assayed like the foregoing, half normal hydrochloric acid V.S.

Each mil of half normal acid V.S. corresponds to 0.05454 gm. of $Ca(C_3H_5O_3)_2$.

Strontium Salicylate ($Sr(C_7H_5O_3)_2 + 2H_2O = 397.74$). This is assayed like the foregoing, but care must be taken not to allow the temperature to exceed red heat during the carbonization. Each mil of half normal hydrochloric acid V.S. corresponds to 0.099435 gm. of $Sr(C_7H_5O_3)_2 + 2H_2O$.

Pulvis Effervescens Compositus (*Seidlitz Powder*). The weight of the mixture in the blue paper should be not less than 9.5 gms. nor more than 10.5 gms. It should contain not less than 23 per cent nor more than 27 per cent of sodium bicarbonate, and not less than 73 per cent nor more than 78 per cent of rochelle salt.

The Assay for Sodium Bicarbonate. Dissolve 2 gms. of the contents of the blue paper in 80 mils of distilled water, add 20 mils of half-normal sulphuric acid V.S., boil the solution until the volume is reduced to about 50 mils and titrate the excess of acid with half-normal potassium hydroxid V.S.,

using phenolphthalein T.S. as indicator. Subtract the number of mils of half-normal potassium hydroxid V.S. used from 20 mils (the quantity of half-normal sulphuric acid taken) and the remainder will be the quantity of the latter which reacted with the sodium bicarbonate.

The calculation is as follows:

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2.$$

$2)168.02$ $\quad$ $2)98.09$

$2)\ 84.01$ $\quad$ $2)49.045$

42.005 $\quad$ 24.522 gms. in 1000 mils of half-normal V.S.

Each mil of half-normal acid V.S. = 0.042005 gm. of $NaHCO_3$.

Assuming that 8 mils of half-normal potassium hydroxid were consumed in the assay then 12 mils of half-normal sulphuric acid reacted with, and hence represent the sodium bicarbonate present.

Hence $0.042 \times 12 = 0.504$ gm. or 25.2 per cent.

The Assay for Rochelle Salt. Take 2 gms. of the contents of the blue paper used in the preceding assay, place it in a porcelain crucible and carbonize it as described under potassium and sodium tartrate. The difference between the number of mils of half-normal sulphuric acid V.S. consumed in this assay and in the preceding assay for sodium bicarbonate multiplied by 0.07055 represents the rochelle salt.

Thus, 50.0 mils of $\frac{N}{2}$ H_2SO_4 V.S. taken

16.5 mils of $\frac{N}{2}$ KOH V.S. required for neutralization

33.5 mils of $\frac{N}{2}$ H_2SO_4 consumed

33.5 mils $-$ 12 mils $=$ 21.5 mils, representing rochelle salt;

$0.07055 \times 21.5 = 1.516$ gm. or 75.8 per cent of crystallized rochelle salt.

Ammonium Benzoate ($NH_4C_7H_5O_2 = 139.08$) and **Ammonium Salicylate** ($NH_4C_7H_5O_3 = 155.08$). It is evident that because of the volatility of ammonia, these salts cannot be assayed by the method employed in the case of organic salts of the fixed alkalies. The official assays of these salts depends upon the liberation of the organic acid, by the addition of sulphuric acid, and its extraction with an immiscible solvent. The solution so obtained is evaporated and the organic acid residue dissolved in neutralized diluted alcohol and titrated with tenth-normal barium hydroxid V.S. The method in detail is as follows: Dissolve about 0.5 gm. of the salt previously dried in a desiccator over sulphuric acid, and accurately weighed, in 10 mils of distilled water, in a separator. Add to the solution 5 mils of diluted sulphuric acid and extract the liberated organic acid by shaking out with three successive portions of 25, 15, and 10 mils respectively of chloroform, passing the chloroform solution through a filter previously moistened with chloroform, and removing any of the organic acid adhering to the stem of the funnel with a few mils of chloroform. Evaporate the chloroform solution at a very low temperature to 5 mils, add 25 mils of diluted alcohol, which has been previously neutralized with $\frac{N}{10}$ KOH V.S. in the presence of phenolphthalein.

Titrate this solution with $\frac{N}{10}$ barium hydroxid V.S., using phenolphthalein as indicator.

Each mil of the $\frac{N}{10}$ $Ba(OH)_2$ V.S. represents benzoic acid, 0.012205 gm.; salicylic acid, 0.013805 gm.; ammonium benzoate 0.013908 gm., and ammonium salicylate 0.015508 gm.

TABLE SHOWING THE NORMAL FACTORS, ETC., OF THE ORGANIC SALTS OF THE ALKALI METALS.

Substance.	Formula.	Molecular Weight.	Equivalent Weight in Carbonate.	Normal Factor.
Lithium benzoate.....	$LiC_7H_5O_2$	127.98	36.94	0.12798
" citrate.....	$Li_3C_6H_5O_7$	209.92	92.35	0.06997
" salicylate.....	$LiC_7H_5O_3$	143.98	36.94	0.14398
Sodium acetate.....	$NaC_2H_3O_2.3H_2O$	136.07	53.0	0.13607
" benzoate.....	$NaC_7H_5O_2$	144.04	53.0	0.14404
" salicylate.....	$NaC_7H_5O_3$	160.04	53.0	0.16004
Potassium acetate.....	$KC_2H_3O_2$	98.12	69.1	0.09812
" bitartrate.....	$KHC_4H_4O_6$	188.14	69.1	0.18814
" citrate.....	$K_3C_6H_5O_7.H_2O$	324.36	207.3	0.10812
" tartrate.....	$K_2C_4H_4O_6\frac{1}{2}H_2O$	235.24	138.2	0.11762
" and sodium tartrate.....	$KNaC_4H_4O_6.4H_2O$	282.20	122.1	0.1411

Estimation of the Salts of the Alkali Earths

Standard solution of hydrochloric or of nitric acid is preferred by many operators for the titration of hydroxids or carbonates of the alkali earths. These acids possess the advantage over most other acids of forming soluble salts. *The hydroxids* may be estimated by any of the indicators, but as they readily absorb CO_2 out of the air they are generally contaminated with more or less carbonate, and the residual method should be used, i.e., a known excess of standard acid should be added, the mixture boiled to expel any trace of CO_2, and titrated with standard alkali.

The carbonates are of course estimated in the same way, as are also the *organic salts* of the *alkali earths*, after ignition. As an example:

One gram of calcium carbonate is mixed with 5 mils of water. An excess of normal hydrochloric acid V.S. is now added, and the solution boiled to drive off the CO_2. Then a few drops of phenolphthalein T.S. are added, and

titrated with $\frac{N}{1}$ alkali V.S. until a faint pink color is obtained.

Note the quantity of $\frac{N}{1}$ alkali used, and deduct this from the quantity of $\frac{N}{1}$ acid first added, and the remainder will represent the amount of acid which combined with the calcium.

Each mil of $\frac{N}{1}$ acid V.S. represents 0.05 gm. of $CaCO_3$.

$$\underset{2)100}{CaCO_3} + \underset{2)72.92}{2HCl} = CaCl_2 + H_2O + CO_2.$$

50 gms. 36.46 gms. or 1000 mils $\frac{N}{1}$ acid V.S.

Assuming that 30 mils of $\frac{N}{1}$ HCl V.S. were added to the 1 gm. of $CaCO_3$, and that 11 mils of $\frac{N}{1}$ KOH V.S. were required to bring the mixture back to neutrality, then 19 mils of $\frac{N}{1}$ HCl were actually required to saturate the $CaCO_3$.

Therefore $0.050 \times 19 = 0.950$ or 95 per cent.

The hydroxids and carbonates may also be estimated by direct titration with standard hydrochloric acid (in the cold) using methyl orange as indicator. A better plan, however, would be to add the standard acid in slight excess, and then standard alkali until a distinct yellow color appears; the slight excess of alkali is then determined by adding standard hydrochloric acid until the red color reappears. A much more distinct color reaction is thereby obtained. The quantity of the standard alkali used is deducted from the total quantity of standard acid added.

Soluble salts of calcium, barium and strontium, such as chlorids, nitrates, etc., may be readily estimated as follows:

A weighed quantity of the salt is dissolved in water, cautiously neutralized if it is acid or alkaline, phenolphthalein is added, the mixture heated to boiling, and standard solution of sodium carbonate delivered in from time to time, with constant boiling until the red color is permanent.

This process depends upon the fact that sodium carbonate forms with soluble salts of these bases insoluble neutral carbonates.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$
$$Ba(NO_3)_2 + Na_2CO_3 = BaCO_3 + 2NaNO_3.$$

As an example of the process: Take of calcium chlorid one gram, dissolve it in a small quantity of water, neutralize the solution if it is acid or alkaline, heat to boiling, add a few drops of phenolphthalein, and titrate with $\frac{N}{1}$ sodium carbonate, delivered cautiously while boiling until the red color is permanent.

$$\underset{2)111}{CaCl_2} + \underset{2)106}{Na_2CO_3} = CaCO_3 + 2NaCl.$$
$$\underset{56.5 \text{ gms.}}{} \qquad \underset{53 \text{ gms. or } 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}{}$$

Each mil of $\frac{N}{1}$ Na_2CO_3 V.S. represents 0.0565 gm. of $CaCl_2$. If 17 mils are used the salt contains 0.0565 gm. $\times$ 17 = 0.96 gm. or 96 per cent.

Normal Sodium Carbonate V.S. ($Na_2CO_3 = 106$) contains 53 gms. in 1 liter. This solution is made by dissolving 53 gms. of pure sodium carbonate (anhydrous) previously ignited and cooled, in distilled water, and diluting to 1 liter at 25° C.

If a pure salt is not at hand the solution may be made as follows:

About 85 gms. of pure sodium bicarbonate, free from thiosulphate, chlorid, etc., are heated to dull redness (not to

fusion) for about thirty minutes to expel one-half of the CO_2; it is then cooled under a desiccator. When cool, 53 gms. are dissolved in distilled water to make 1 liter at 25° C. (77° F.). This solution should neutralize $\frac{N}{1}$ acid V.S. volume for volume.

The alkali earths may also be estimated by dissolving them in water, precipitating the base as carbonate, with an excess of ammonium carbonate and some free ammonia. The mixture is then heated for a few minutes, and the carbonate separated by filtration, thoroughly washed with hot water till all soluble matters are removed, and then titrated with normal acid V.S. as directed for carbonate.

$$\underset{\substack{2)198.52\\ 99.26 \text{ gms.}}}{CaBr_2} = \underset{\substack{2)99.35\\ 49.675 \text{ gms.}}}{CaCO_2} = \underset{\substack{2)98\\ 49 \text{ gms. or 1000 mils } \frac{N}{1} \text{ V.S.}}}{H_2SO_4}.$$

Each mil of $\frac{N}{1}$ acid thus represents 0.09926 gm. of $CaBr_2$.

Another method for the estimation of salts of the alkali earths consists in precipitating them as oxalates out of an ammoniacal or weak acetic acid solution. The precipitated oxalate is then, after thorough washing, titrated with tenth-normal potassium permanganate V.S. Or the excess of oxalic acid in the filtrate may be titrated with standard permanganate V.S. This method is, however, especially applicable to calcium estimations because of the completeness with which this metal may be precipitated as oxalate.

Magnesium Carbonate. One gm. of magnesium carbonate is dissolved in 30 mils of normal sulphuric acid V.S., and the excess of the latter determined by titration with normal potassium hydroxid V.S., using methyl orange as indicator. **Magnesium Oxid** and **Magnesium Hydroxid** are estimated in

exactly the same manner. The absence of calcium oxid must, however, be assured, or, if present, its quantity determined.

This is done by precipitation with ammonium oxalate in the presence of ammonium chlorid and ammonium hydroxid. The precipitate is incinerated and the residual calcium oxid weighed.

Alkalimetric Assay of Zinc Salts. *Zinc Oxid.* Digest about 1.5 gm. of zinc oxid, accurately weighed, with 50 mils of normal sulphuric acid V.S., until solution is complete. Then titrate the excess of sulphuric acid with normal potassium hydroxid V.S., using methyl orange as indicator.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$

Zinc carbonate and zinc stearate are assayed in the same manner. In the case of the latter, boiling for ten minutes may be necessary in order to completely dissolve the salt. Each mil of normal sulphuric acid V.S. corresponds to 0.040685 gm. of zinc oxid.

The Estimation of Mixed Hydroxids and Carbonates of Alkali Earths. This may be done as described under estimation of mixed alkali hydroxids and carbonates, page 77, except that in this case it is unnecessary to precipitate the carbonate by barium chlorid in that the alkali earth carbonates are already insoluble.

Assay of Chloral Hydrate. Dissolve an accurately weighed quantity (about 4 gms.) of chloral hydrate in 10 mils of distilled water, add 30 mils of normal potassium hydroxid V.S., and let the solution stand about two minutes. Then add phenolphthalein T.S., and at once titrate the excess of alkali by means of normal sulphuric acid V.S.

This reaction must take place in the cold or at least at ordinary temperature, otherwise the alkali will attack the chloroform which is formed and yield too high results. The

chloroform liberated produces a slight turbidity which may be dissipated by swinging the flask for a minute or two.

The reaction is thus expressed:

$$\underbrace{C_2HCl_3O + H_2O}_{165.4} + KOH = CHCl_3 + HCOOK + H_2O.$$

Each mil of normal alkali consumed corresponds to 0.1654 gm. of $C_2HCl_3O + H_2O$.

Acidimetry

The Estimation of Acids by Neutralization. In the preceding pages it has been shown how alkalies are estimated by the

Fig. 35.

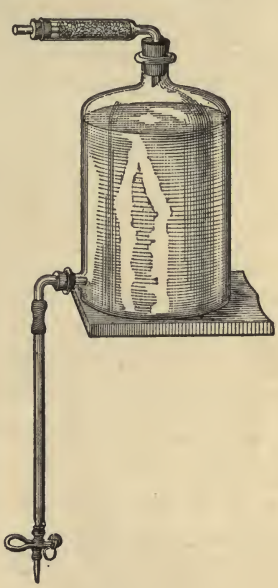

Fig. 36.

use of acid solutions of known neutralizing power. In the estimation of acids, which will now be described, the order

is reversed, alkaline solutions of known power being used in determining the strength of acids and of acid salts. Thus the procedure is analogous to that of the alkalimetric methods. The choice of the indicator, whether litmus, phenolphthalein, or methyl orange, depends upon the particular acid to be estimated. Phenolphthalein is employed for the organic acids and boric acid and is preferred for phosphoric acid; while methyl orange and litmus are usually employed in the titration of the inorganic acids.

The standard alkali used may be either an hydroxid or a carbonate, the former is, however, usually preferred, because the carbonate when brought in contact with an acid gives off carbonic acid gas (CO_2) which interferes to a great extent with most indicators. On the other hand, it must be remembered that the alkali hydroxids are very prone to absorb carbon dioxid from the atmosphere, therefore their solutions often contain some carbonate, the presence of which even in small quantities will occasion errors when used with most indicators, especially with litmus and phenolphthalein. It is therefore advisable, when using these indicators or others which are affected by carbon dioxid, to employ gentle heat toward the close of each titration, in order to drive off the liberated gas. Methyl orange is not affected by this gas, and therefore heating is not necessary when this indicator is used. In fact, it is imperative that heat should not be employed with this indicator.

In acidimetrical operations when methyl orange is used as indicator, residual titrations may be advantageously done, because the change of color from yellow to red which is brought about by the acid is much more readily seen than that from red to yellow.

In the U. S. P. standard solutions of both potassium and sodium hydroxid are official. The former, however, is pref-

erable, because it attacks glass less energetically, and also foams much less than does the sodium hydroxid solution. The neutralizing power of both is, however, the same. Standard solutions of alkali hydroxid should be preserved in small vials, provided with well-fitting rubber stoppers, or better still, they should be provided with tubes filled with a mixture of soda and lime, which absorbs CO_2 and prevents its access to the solution. A vessel of this description is illustrated in Fig. 35.

An improvement upon this is shown in Fig. 36, since it allows of the burette being filled without removing the stopper, and consequently without any access of CO_2 whatever.

Where a series of titrations of the same kind have to be made with the same alkali standard solution, the arrangement shown in Fig. 9 may be used, both the reservoir and the burette in this case being provided with soda-lime tubes.

Preparation of Standard Alkali Solutions

Normal Potassium Hydroxid V.S. ($KOH = 56.11$; $\frac{N}{1}$ V.S. $= 56.11$ gms. in 1000 mils). Potassium hydroxid being prone to absorb carbon dioxid out of the air the pure article is not readily obtained in commerce. If pure potassium hydroxid were easily obtained it would only be necessary to dissolve 56.1 gms. in sufficient water to make 1000 mils. But since it always contains some CO_2 and H_2O, it is necessary to take a slight excess and dilute the solution to the proper volume after having determined its strength.

The standardization may be effected by means of any of the standard acid solutions.

A satisfactory method for the preparation and standardization of this solution is as follows:

Dissolve 75 gms. of potassium hydroxid in sufficient recently

boiled distilled water to make about 1050 mils at 25° C. (77° F.), and fill a burette with a portion of this solution.

Dissolve 0.63 gm. of pure oxalic acid in about 10 mils of water in a beaker or flask, add a few drops of phenolphthalein T.S., and then carefully add from the burette the potassium hydroxid solution, agitating frequently and regulating the flow to drops towards the end of the operation until a permanent pale pink color is obtained. Note the number of mils of the alkali solution consumed, and then dilute the remainder so that exactly 10 mils of the diluted liquid will be required to neutralize 0.63 gm. of oxalic acid. Instead of weighing off 0.63 gm. of the acid, 10 mils of its normal solution may be used.

Example. Assuming that 8 mils of the stronger potassium hydroxid solution had been consumed in the trial, then each 8 mils must be diluted to 10 mils, or the whole or the remaining solution in the same proportion. Thus if 8 mils must be diluted to 10 mils, 1000 mils must be diluted to 1250 mils.

$$8 : 10 :: 1000 : x \qquad x = 1250 \text{ mils.}$$

It is always advisable to make another trial after diluting. Ten mils should then neutralize 0.63 gm. of pure oxalic acid.

Standardization by Means of Potassium Bitartrate. This method is based upon the reaction

$$\underset{188.14}{KHC_4H_4O_6} + \underset{56.1}{KOH} = K_2C_4H_4O_6 + H_2O.$$

1000 mils of $\frac{N}{1}$ KOH contains 56.11 gms. of KOH and will react with 188.14 gms. of potassium bitartrate. 25 mils of $\frac{N}{1}$ KOH will therefore react with 4.7035 gms. of potassium bitartrate.

A solution of potassium hydroxid, 75 gms. in 1050 mils, is

prepared and titrated against pure potassium bitartrate, using phenolphthalein as indicator.

Into a flask of about 300 mils capacity introduce 4.7035 gms. of purified dry potassium bitartrate,* followed by 15 mils (accurately measured at 25° C.) of the potassium hydroxid solution which is being prepared and 80 mils of distilled water. Heat the solution to boiling, add from 3 to 5 drops of phenolphthalein T.S. and then cautiously add from a burette further portions of the potassium hydroxid solution. Agitate the flask frequently, boil the liquid toward the end of the operation and reduce the flow of the potassium hydroxid solution to drops until the red color produced by its influx no longer disappears on shaking and the liquid is not deeper in color than a pale pink. Note the number of mils of the potassium hydroxid solution consumed and then dilute the remainder of the solution so that exactly 25 mils of the diluted liquid at standard temperature shall be required to neutralize the 4.7035 gms. of potassium bitartrate. If only 22 mils are consumed in the trial, then each 22 mils must be diluted to 25 mils or the whole of the remaining solution in the same proportion.

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* Purified potassium bitartrate for standardizing caustic alkali volumetric solutions may be obtained as follows: 100 gms. of the salt are placed in a beaker, together with 85 mils of water and 25 mils of 10 per cent hydrochloric acid, the beaker is covered and heated on a boiling water-bath, stirring occasionally for three hours. The liquid is then quickly cooled, decanted, and the residue washed first by decantation with 100 mils of cold water, then again washed after it has been transferred to a plain filter, using cold water until the filtrate ceases to become opalescent when acidified with a few drops of nitric acid upon the addition of silver nitrate solution. The precipitate is then dissolved in the smallest possible quantity of boiling water (about 1500 mils) filtered, and the filtrate stirred constantly while cooling. When cold, the crystalline precipitate is collected upon a filter washed with 300 mils of cold water, run through it in small portions at a time. It is then allowed to drain, and finally dried in an air oven at 120° C. until its weight is constant.

Standardization by Means of Potassium Bi-iodate.* Potassium bi-iodate is an acid salt and may be directly titrated with potassium hydroxid, using phenolphthalein as indicator.

One molecule of the bi-iodate is equivalent to one molecule of potassium hydroxid, as shown by the equation,

$$\underset{389.94}{KH(IO_3)_2} + \underset{56.11}{KOH} = 2KIO_3 + H_2O.$$

To standardize a potassium-hydroxid solution, weigh accurately 3.8994 gms. of potassium bi-iodate, dissolve it in about 25 mils of water, add a few drops of phenolphthalein, and then run into this, from a burette, the hydroxid solution which is to be standardized, until a pale pink color appears. Note the number of mils used and dilute the solution so that exactly 10 mils of it will neutralize 3.8994 gms. of the bi-iodate.

Example. Assuming that 8.2 mils had been consumed, then each 8.2 mils must be diluted to 10 mils, or the whole of the remaining solution in the same proportion.

The advantages of this salt as an ultimate standard are (1) that it may be procured in the market in a state of absolute purity;† (2) that it is permanent, being neither deliquescent nor efflorescent; (3) that it can be dried at 110° C. without decomposition; (4) that the results obtained with it are quite accurate, and (5) that it may be employed for standardizing most of the volumetric solutions commonly found in the laboratory.

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* See Meinecke, Chem. Ztg., XIX. 2. Also Caspari, Proc. A. Ph. A., 1904, 389.

† According to Caspari, the salt may be readily prepared as follows: See A. Ph. A., 1904, 390. Potassium bicarbonate is mixed in solution with an equivalent amount of iodic acid, and to the neutral solution is added an amount of iodic acid equal to the quantity first used. The solution is then evaporated until crystallization begins, and the first crop of crystals rejected. Those which separate after the solution has cooled to 50° C. are almost pure and will be rendered absolutely pure if recrystallized.

Standardization by Means of Normal Acid V.S. 20 mils of a strictly normal acid V.S. are placed into a beaker, 2 drops of methyl orange T.S. are added and the potassium hydroxid solution delivered into it until the red liquid just turns yellow. If the alkali hydroxid solution is strictly normal, there will be consumed exactly 20 mils. If less is consumed the solution is too strong and must be so diluted with distilled water that equal volumes of it and the normal acid will exactly neutralize each other. Thus if 18 mils of the alkali are consumed, then each 18 mils must be diluted to 20 mils.

Normal Sodium Hydroxid V.S. ($NaOH = 40$; $\frac{N}{1}$ V.S. $= 40$ gms. in 1000 mils). Dissolve 54 gms. of sodium hydroxid in enough recently boiled distilled water to make about 1050 mils of solution, fill a burette with a portion of this, and check it with normal acid, or a weighed quantity of oxalic acid or potassium bitartrate, in exactly the same manner as described for normal potassium hydroxid.

Other strengths of standard alkali V.S. are half-normal $\left(\frac{N}{2}\right)$, Fifth-normal, $\left(\frac{N}{5}\right)$, Tenth-normal $\left(\frac{N}{10}\right)$, Twentieth-normal $\left(\frac{N}{20}\right)$, Fiftieth-normal $\left(\frac{N}{50}\right)$, Hundredth-normal $\left(\frac{N}{100}\right)$. These are all prepared by properly diluting the normal V.S. and then checking the strength of the product.

Other standard alkali solutions in frequent use are normal sodium carbonate, normal and other strengths of ammonia, and tenth-normal barium hydroxid.

Tenth Normal Barium Hydroxid V.S. ($Ba(OH)_2 + 8H_2O = 315.51$ $\frac{N}{10}$ V.S. $= 15.776$ gms. in 1000 mils). Dissolve about 18 gms. of crystallized barium hydroxid in 1000 mils of recently boiled distilled water, and, if necessary, filter the solution quickly.

Introduce 25 mils of tenth-normal hydrochloric acid V.S. into a flask, add 3 drops of phenolphthalein T.S. and run in the barium hydroxid solution from a burette, provided with a soda-lime tube, reducing the flow to drops toward the end until a pale pink color is obtained which does not disappear on shaking the liquid for ten seconds. Note the number of mils consumed and if the solution is too concentrated, dilute the remainder with freshly boiled and cooled distilled water, so that equal volumes of the barium hydroxid solution and of tenth-normal hydrochloric acid V.S. at 25° C. exactly neutralize each other.

NOTE. This solution absorbs CO_2 from the air very rapidly, and thereby loses its titer. It should therefore be preserved in rubber-stoppered bottles provided with a soda-lime tube. (See Fig. 35.) This solution must be standardized each time before using.

Estimation of the Inorganic Acids

To weigh off directly a definite quantity of a fluid acid, is not a very easy matter. It is always a better plan to measure a small quantity of the acid and weigh it accurately in a tared and stoppered weighing flask (Fig. 37), then to add water and titrate with the standard alkali in the presence of a suitable indicator. If the specific gravity of the acid is known or can be easily taken, it is sufficient to measure a certain quantity of it by means of a pipette, and then determine its weight by multiplying the volume in cubic centimeters by the specific gravity. It must be remembered, however, that the liquid must be measured at the same temperature at which the specific gravity was taken. This method is applicable to the diluted acids as well as to the concentrated acids of commerce, as hydrochloric, nitric and sulphuric.

FIG. 37.

In the case of very volatile acids, i.e., such as evolve acid vapors at ordinary temperatures, the determination of the weight by means of the specific gravity is inadmissable. Such acids should be weighed in a Lunge pipette, Fig. 38, or in a simple bulb pipette provided with a glass stop-cock, Fig. 39, or in a Grethan's pipette, Fig. 40.

The Lunge pipette is used by producing a vacuum in the bulb (*a*), the air-tight glass mantle (*c*) is then removed,

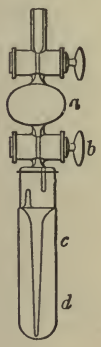

Fig. 38.

Fig. 39.

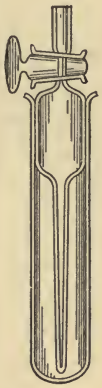

Fig. 40.

and the tip of the tube (*d*) sunk into the acid which is drawn up into the bulb, upon opening the cock (*b*); when sufficient of the acid has been drawn into the apparatus the cock is closed, the tip of the pipette wiped, the glass mantle put in place, and the whole weighed. The weight of the empty pipette deducted gives the weight of the acid taken up. The pipettes shown in Figs. 39 and 40 are filled by applying direct suction with the lips, the operator protecting himself against inhalation of harmful vapors by attaching an absorption tube containing soda-lime, caustic soda, or similar substance.

The quantity of acid to be taken (in most cases) should be such as will require for neutralization from 20 to 50 mils of the standard alkali. In the case of concentrated inorganic acids, 2 or 3 gms. may be taken, while in the case of the dilute acids, from 6 to 8 gms.

Any of the indicators may be employed for the inorganic acids, but because of the usual presence of carbonate in the standard alkali, methyl orange is preferred.

Hydrochloric Acid ($HCl = 36.47$). About 2 mils of hydrochloric acid (sp.gr. 1.155) are introduced into a tared weighing flask and its weight accurately taken. (The weight is found to be 2.098 gms.) Fifty mils of water are now added, followed by 2 drops of methyl orange, and the solution carefully titrated with normal potassium hydroxid until the reddish color of the solution is changed to yellow.

Assuming that 18.4 mils were required, then 18.4 mils $\times$ 0.03647 gm. $=$ 0.671 gm. of absolute hydrochloric acid in the 2.098 gms. taken.

To find the per cent apply the proportion

$$2.098 \text{ gms.} : 0.671 \text{ gm.} :: 100 : x. \qquad x = 31.9 \text{ per cent.}$$

The equation is:

$$HCl + KOH = KCl + H_2O.$$

$$36.47 \text{ gms.} = 56.1 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}$$

$$.03647 \text{ gm.} = 1 \text{ mil } \frac{N}{1} \text{ V.S.}$$

Sulphuric Acid ($H_2SO_4 = 98.09$). About 1 mil of the concentrated acid is weighed in a tared weighing flask and found to weigh 1.8 gms. Fifty mils of water are added and then 2 drops of methyl orange, and the titration with normal potassium hydroxid begun, and cautiously continued until the

yellowish color of the solution indicates the completion of the operation. Note the number of mils of alkali solution used and apply the equation

$$\underset{2)98.09}{H_2SO_4} + \underset{2)112.2}{2KOH} = K_2SO_4 + 2H_2O.$$

$$49.04 \text{ gms.} = 56.1 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}$$

Thus each mil of normal KOH V.S. represents 0.04904 gm. of pure H_2SO_4.

Aromatic Sulphuric Acid. This is an alcoholic solution containing free sulphuric acid and ethyl sulphuric together with a volatile dil. The latter as well as the alcohol present neutralizes alkali hydroxid, and must therefore be removed by heating before titration of the acid is undertaken. The U.S.P. method is as follows: Pour about 10 mils of aromatic sulphuric acid into a tared flask, stopper and weigh, transfer to a small flask using 60 mils of distilled water to rinse the weighing-flask, and, having connected the flask with a reflux condenser, boil the liquid for six hours; when cold, dilute it with distilled water to about 100 mils, and titrate with normal potassium hydroxid V.S., using methyl orange as indicator. Calculate as in preceding assay.

Phosphoric Acid ($H_3PO_4 = 98.064$). In the assay of phosphoric acid by direct neutralization with standard KOH, the acid is converted into, first, KH_2PO_4, then K_2HPO_4, and finally into the normal K_3PO_4. We have no indicator which reliably shows the completion of the neutralization, i.e., the formation of the tribasic K_3PO_4. Litmus cannot be used as indicator here for the dipotassic or disodichydric phosphate (K_2HPO_4 or Na_2HPO_4) which is formed is slightly alkaline towards litmus; the same is true of most other indicators.

Thompson, however, has demonstrated that this acid may

be accurately titrated by standard alkali when using either methyl orange or phenolphthalein, or both, successively.

If methyl orange is used the color changes upon the completion of the formation of monobasic phosphate, KH_2PO_4, as per the following equation:

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O.$$

If phenolphthalein is used, the color changes upon the completion of the formation of the dibasic phosphate, K_2HPO_4,

$$H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O.$$

As an example: A weighed quantity of the acid is diluted with water to measure 20 mils and sufficient pure sodium chlorid added to saturate the solution. Four drops of methyl orange are then introduced and the titration with $\frac{N}{1}$ KOH begun and continued until the red color changes to yellow, indicating the formation of the monobasic phosphate

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O.$$
$$98.064 \text{ gms.} \quad 56.1 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}$$

Each mil of $\frac{N}{1}$ KOH V.S. = 0.098064 gm. of H_3PO_4.

The use of sodium chlorid in this assay is to decrease the ionization of the acid salts produced in the reaction.

Another portion of the acid is treated in like manner, adding sodium chlorid and titrating, but using phenolphthalein as the indicator. The titration is continued until a faint permanent pink color appears. It is advisable to use heat, or better still, a standard alkali solution which is quite free

from CO_2. The end-reaction in this case marks the formation of the dibasic phosphate

$$\underset{2)98.064}{H_3PO_4} + \underset{2)112.2}{2KOH} = K_2HPO_4 + 2H_2O.$$
$$\underset{49.032 \text{ gms.}}{} \qquad \underset{56.1 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}{}$$

Each mil of $\frac{N}{1}$ KOH V.S. = 0.049032 gm. of H_3PO_4.

Just twice as much of the $\frac{N}{1}$ KOH V.S. will be taken in this assay as in the foregoing.

The two assays may be combined as follows: A weighed quantity of the acid is diluted with water saturated with sodium chlorid and titrated with the normal alkali V.S., using methyl orange as indicator until the red color of the solution changes to yellow. The number of mils is noted and multiplied by 0.098064 gm. A few drops of phenolphthalein solution are now added and the titration continued until a pale-red color appears. The total number of mils of normal alkali used in the double titration is then multiplied by 0.049032 gm.

The U.S.P. method for the assay of phosphoric acid is given on page 127.

Hypophosphorous Acid ($HPH_2O_2 = 66.06$).

$$HPH_2O_2 + KOH = KPH_2O_2 + H_2O.$$

Each mil of $\frac{N}{1}$ alkali represents 0.06606 gm. of HPH_2O_2.

Nitric Acid ($HNO_3 = 63.02$).

$$HNO_3 + KOH = KNO_3 + H_2O.$$

Each mil of $\frac{N}{1}$ alkali represents 0.06302 gm. of HNO_3.

Hydrobromic and hydriodic acids may be estimated in

the same way as the foregoing, but it is usually preferred to estimate them by precipitation analysis. This is also true of phosphoric acid. Sulphurous acid is best assayed by oxidation with iodin.

Boric Acid ($H_3BO_3 = 62.02$). This acid is estimated by neutralization with $\frac{N}{1}$ NaOH in the presence of a large quantity of glycerin. (Thompson's Method, J. S. C. I., XII, 432). The addition of sufficient glycerin to a boric acid solution, so that no less than 30 per cent be present throughout the titration, develops the acidity of boric acid with regard to phenolphthalein to a great degree, and enables one to titrate direct with standard soda solution. One gm. of boric acid is dissolved in 50 mils of water; to this is added an equal volume of glycerin, then a few drops of phenolphthalein, and the titration with normal sodium hydroxid begun and continued until a pink color appears.

Each mil of $\frac{N}{1}$ NaOH = 0.06202 gm. of H_3BO_3.

$$H_3BO_3 + NaOH = NaH_2BO_3 + H_2O.$$

62.02 40 gms. in 1000 mils $\frac{N}{1}$ V.S.

0.06202 gm. = 1 mil $\frac{N}{1}$ V.S.

Estimation of the Organic Acids

As the individual organic acids require different indicators, the table on page 28 should be consulted in the selection of an indicator for a particular organic acid. Phenolphthalein is, however, the most suitable for organic acids generally.

Acetic Acid ($HC_2H_3O_2 = 60.03$). Mix 3 gms. of the acid with 50 mils of water, add a few drops of phenolphthalein T.S., and titrate with normal potassium hydroxid V.S. until

a permanent pale pink color is obtained, and apply the following equation:

$$\underset{60}{HC_2H_3O_2} + \underset{56.1}{KOH} = KC_2H_3O_3 + H_2O.$$

Thus 1000 mils of $\frac{N}{1}$ KOH V.S. will neutralize 60 gms. of acetic acid; therefore each mil of $\frac{N}{1}$ KOH V.S. represents 0.060 gm. of acetic acid.

If 18 mils are required to neutralize 3 gms. of the acid, it contains $18 \times 0.06 = 1.08$ gms. of absolute acetic acid.

$$\frac{1.08 \times 100}{3} = 36 \text{ per cent.}$$

Tartaric Acid ($H_2C_4H_4O_6 = 150.05$). Dissolve 2 gms. of tartaric acid in 50 mils of distilled water, add a few drops of phenolphthalein and then pass into the solution from a burette $\frac{N}{1}$ potassium hydroxid V.S. until a faint pink tint is acquired by the solution, and apply the equation

$$\underset{\substack{2)150 \\ 75 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}}{H_2C_4H_4O_6} + 2KOH = K_2C_4H_4O_6 + 2H_2O.$$

Citric Acid ($H_3C_6H_5O_7 = 192.06$).

$$\underset{\substack{3)192.06 \\ 64.01 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.}}}{H_3C_6H_5O_7} + 3KOH = K_3C_6H_5O_7 + 4H_2O.$$

Each mil of $\frac{N}{1}$ KOH represents 0.06401 gm. of citric acid.

Trichloracetic Acid ($CCl_3COOH = 163.39$).

$$\underset{163.39}{CCl_3COOH} + KOH = CCl_3COOK + H_2O.$$

Each mil of $\frac{N}{1}$ KOH V.S. represents 0.16339 gm. of trichloracetic acid.

The other organic acids are assayed in exactly the same manner as that described for the foregoing with the exception of benzoic and salicylic acids.

Benzoic Acid ($HC_7H_5O_2$) and **Salicylic Acid** ($HC_7H_5O_3$). These acids are assayed as follows: Dissolve 0.5 gm. of the acid, previously dried to constant weight in a desiccator over sulphuric acid, in 25 mils of diluted alcohol which has been previously neutralized with tenth-normal potassium hydroxid V.S., phenolphthalein T.S. being used as indicator. Titrate this solution with tenth-normal barium hydroxid V.S.,* using phenolphthalein as indicator.

The reactions are

$$2HC_7H_5O_2 + Ba(OH)_2 = Ba(C_7H_5O_2)_2 + 2H_2O.$$

$$2)244.10$$
$$10)122.05$$
$$12.205 = \text{to } 1000 \text{ mils } \frac{N}{10} Ba(OH)_2 \text{ V.S.}$$

Each mil of $\frac{N}{10}$ $Ba(OH)_2$ V.S. represents 0.012205 gm. of benzoic acid and 0.013805 gm. of salicylic acid.

Lactic Acid ($HC_3H_5O_3 = 90.05$). A definite weight is treated with an excess of normal potassium hydroxid V.S. and boiled for twenty minutes. The boiling solution is then titrated with normal sulphuric acid V.S. The quantity of the latter consumed deducted from the quantity (in mils) of normal potassium hydroxid V.S. originally added, gives the quantity of the alkali solution which represents the lactic acid being assayed.

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* See page 101.

TABLE SHOWING QUANTITY OF SUBSTANCE TO BE TAKEN FOR ANALYSIS IN DIRECT PERCENTAGE ESTIMATIONS.

	Molecular Weight.	Quantity to be taken so that each mil of $\frac{N}{1}$ V.S. will represent 1 %.	Percentage strength of Official Substance.
Acid, acetic, $HC_2H_3O_2$	60.03	6.03 gms.	36.
" boric, H_3BO_3	62.02	6.2 "	99.5
" citric, $H_3C_6H_5O_7+H_2O$	210.08	7.0 "	99.5
" hydrobromic, HBr. Dil	80.93	8.093 "	10.
" hydrochloric, HCl	36.47	3.647 "	32.
" hydriodic, HI. Dil	127.93	12.793 "	10.
" hypophosphorous, HPH_2O_2	66.04	6.604 "	30.
" lactic, $HC_3H_5O_3$	90.05	9.0 "	85.
" nitric, HNO_3	63.01	6.301 "	68.
" oxalic, $H_2C_2O_4+2H_2O$	126.05	6.3 "	
" phosphoric, H_3PO_4	98.06	.....	85.
" phosphoric with methyl orange	.....	9.806 "	
" phosphoric with phenolphthalein	.....	4.903 "	
" sulphuric, H_2SO_4	98.09	4.903 "	94.
" tartaric, $H_2C_4H_4O_6$	150.05	7.5 "	99.5
" trichloracetic, $HC_2Cl_3O_2$	163.38	1.6338 "	99.
Ammonium carbonate, $N_3H_{11}C_2O_5$	157.11	5.25 "	
Ammonia water, NH_3	17.03	1.7 "	10.
Ammonia water, stronger, NH_3	17.03	1.7 "	28.
Lime water, $Ca(OH)_2$	74.09	3.704 "	0.14
Lithium carbonate, Li_2CO_3	73.88	3.69 "	98.5
" citrate, $Li_3C_6H_5O_7+4H_2O$	281.92	9.397 "	98.5
Potassium acetate, $KC_2H_3O_2$	98.12	9.812 "	99.
" bicarbonate, $KHCO_3$	100.1	10.01 "	99.
" bitartrate, $KHC_4H_4O_6$	188.1	18.81 "	99.5
" carbonate, K_2CO_3	138.2	6.91 "	99.
" citrate, $K_3C_6H_5O_7+H_2O$	324.36	10.81 "	99.
" hydroxid, KOH	56.1	5.61 "	85.
" hydroxid, liquor, KOH	56.1	5.61 "	4.5
" sodium tartrate $KNaC_4H_4O_6+4H_2O$	282.2	14.10 "	99.
Sodium acetate, $NaC_2H_3O_2+3H_2O$	136.0	13.6 "	99.5
" benzoate, $NaC_7H_5O_2$	144.0	14.4 "	99.
" bicarbonate, $NaHCO_3$	84.0	8.4 "	99.
" carbonate, Na_2CO_3	106.0	5.3 "	

Referring to the table it will be seen that if the quantities indicated are taken for analysis, the amount of standard solution required for substances of high percentage strength will be very large (in some cases over 99 mils), while for sub-

stances of low percentage strength, as for instance lime water, so small a volume of standard solution is required as to be unreadable (0.14 mil). It is therefore advisable to take for analysis a smaller quantity of high percentage substances and a larger quantity of such substances as contain a low percentage. It is usually best to so adjust it that no less than 10 nor more than 30 mils of the standard solution be required. For example: In the case of citric acid, instead of taking for analysis 7 gms. it will be better to take one-fourth of this quantity, then each mil of the standard solution used will represent 4 per cent, and only one-fourth as much will be required, i.e., 24.9 mils instead of 99.5 mils. Again, in the case of lime water, if 37.04 gms. are taken instead of 3.704 gms., 1.4 mils of the $\frac{N}{1}$ standard solution will be required, which is better than 0.14 mil, but in this case it will be still better to use a decinormal $\left(\frac{N}{10}\right)$ solution, then 37.04 gms. of lime water would require for neutralization just 14 mils of the $\frac{N}{10}$ acid V.S.

If half the quantity indicated in the table is taken, then each mil of the standard solution would represent 2 per cent. If one-tenth the quantity is taken each mil will represent 10 per cent. If double the quantity is taken each mil will represent 0.5 per cent, etc.

CHAPTER IX

ANALYSIS BY PRECIPITATION

THE general principle of this method is that the determination of the quantity of a given substance is effected by the formation of a precipitate, upon the addition of the standard solution to the substance under examination. There are three ways of determining the end-reaction in precipitation analyses:

1. *By adding the standard solution until it ceases to produce any more precipitate*, as in the estimation of silver by standard sodium chlorid, and the estimation of haloid salts and acids by means of standard silver nitrate. The application of this ending is almost limited to the above estimations, because in these only can accurate results be obtained. The silver halids formed are not only quite insoluble, but they have a tendency to curdle closely upon shaking (especially in acid solutions), and thus leave a clear supernatant liquid in which any further precipitation can readily be seen. Most of the other precipitates, such as barium sulphate, calcium oxalate, etc., although heavy and insoluble, are so finely divided and powdery that they do not readily subside.

2. *By the use of an indicator*, as in the estimation of haloid salts by means of standard silver nitrate solution, using neutral potassium chromate as the indicator. The latter is added to the haloid solution (which must be neutral), and the silver nitrate V.S. delivered into the mixture until a permanent red color (silver chromate) is produced. Silver nitrate reacts by preference with the halogen, and does not react with the chro-

mate until the halogen has been entirely precipitated. Hence the production of a permanent red color in the precipitate marks the completion of the precipitation of the halogen.

Another illustration is in the estimation of silver by sulphocyanate solution, using ferric alum as indicator. The sulphocyanate produces with the silver a white precipitate of silver sulphocyanate, but when the precipitation of silver is complete the sulphocyanate reacts with the ferric alum present and a red ferric sulphocyanate appears and marks the end-point. On the other hand, the indicator may be used externally, i.e., alongside of the liquid being analyzed, a drop of the latter being brought in contact with a drop of the indicator at frequent intervals in the course of the titration, as in the estimation of phosphoric acid by means of uranium nitrate solution, in which potassium ferrocyanide is used as indicator.

3. *By adding the standard solution until the first appearance of a precipitate*, as in the estimation of cyanogen by silver nitrate solution, and the estimation of chlorin by mercuric nitrate V.S. In these estimations the standard solution is added to the solution of the substance under analysis until a precipitate appears.

Preparation of Decinormal $\left(\frac{N}{10}\right)$ Silver Nitrate ($AgNO_3 = 169.89$; $\frac{N}{10}$ V.S. = 16.989 gms. in 1000 mils). Dissolve 16.989 gms. of pure silver nitrate* in sufficient water to make, at or near 25° C. (77° F.), exactly 1000 mils. One liter of this solution thus contains $\frac{1}{10}$ of the molecular weight in grams of silver nitrate. It is therefore a decinormal solution.

If pure crystals of silver nitrate are not readily obtainable, and pure sodium chlorid is at hand, a solution of the silver

* This should be pulverized and dried at 120° C. for half an hour in a covered crucible before weighing.

nitrate may be made of approximate strength, a little stronger than necessary, and then standardized by means of the sodium chlorid, as follows: 0.11692 gm. of sodium chlorid is dissolved in distilled water, and a burette filled with the solution of silver nitrate to be standardized. The silver solution is now slowly added from the burette to the sodium chlorid solution contained in a beaker until no more precipitate of silver chlorid is produced.

If neutral potassium chromate is used as an indicator, the end of the reaction is shown by the appearance of yellowish-red silver chromate. This indication is extremely delicate. The silver nitrate does not act upon the chromate until all of the chlorid is converted into silver chlorid.

In the above reaction 20 mils of silver nitrate should be required. But since the silver nitrate solution is too strong, less of it will complete the reaction, and the solution must be diluted so that exactly 20 mils will be required to precipitate the chlorin in 0.11692 gm. of NaCl.

Thus if 17 mils are used, each 17 mils must be diluted to 20 mils, or each 170 mils to 200 mils, or the entire remaining solution in the same proportion.

After dilution a fresh trial should always be made.

Silver nitrate solution should be kept in dark amber-colored, glass-stoppered bottles, carefully protected from dust.

The U.S.P. IX directs the use of pure metallic silver (foil, wire, or powder) for preparing this solution. Into a flask containing 10.788 gms. of pure silver introduce gradually about 30 mils of nitric acid (sp.gr. about 1.403 at 25° C.) or sufficient for complete solution. Thoroughly rinse the neck of the flask and the funnel which is used. Evaporate the solution to dryness, carefully protecting it from dust. Then, after drying in an air oven at about 120° C., for ten minutes, dissolve the

residue in sufficient distilled water to measure exactly 1000 mils at 25° C.

Decinormal $\frac{N}{10}$ Sodium Chlorid (NaCl = 58.46; $\frac{N}{10}$ V.S. = 5.846 gms. in 1000 mils). Dissolve 5.846 gms. of pure sodium chlorid in enough water to make exactly 1000 mils at the standard temperature.

Check this solution with decinormal silver nitrate. The two solutions should correspond, volume for volume.

Pure Sodium Chlorid may be prepared by passing into a saturated aqueous solution of the purest commercial sodium chlorid a current of dry hydrochloric acid gas. The crystalline precipitate is then separated and dried at a temperature sufficiently high to expel all traces of free acid.

The method of standardizing $\frac{N}{10}$ NaCl solution is as follows: 0.33978 gm. of silver nitrate is dissolved in 10 mils of distilled water, and the solution carefully titrated with $\frac{N}{10}$ NaCl V.S. until precipitation ceases. Twenty mils of the standard solution should be required.

$$\underset{10)169.89}{AgNO_3} + \underset{10)58.46}{NaCl} = AgCl + NaNO_3.$$

16.989 gms. 5.846 gms., or 1000 mils $\frac{N}{10}$ NaCl V.S.

Each mil of the standard solution represents 0.016989 gm. of pure $AgNO_3$.

$$0.016989 \times 20 = 0.33978 \text{ gm.}$$

$$\frac{0.33978 \times 100}{0.33978} = 100 \text{ per cent.}$$

This solution may also be standardized by residual tiration with Volhard's solution.

Decinormal $\frac{N}{10}$ Potassium Sulphocyanate (Volhard's Solution) (KSCN = 97.18; $\frac{N}{10}$ V.S. = 9.718 gms. in 1000 mils). Dissolve 10 gms. of pure crystallized potassium sulphocyanate (thiocyanate) in 1000 mils of water.

This solution, which is too concentrated, must be adjusted so as to correspond exactly in strength with decinormal silver nitrate V.S. For this purpose introduce into a flask 20 mils of $\frac{N}{10}$ $AgNO_3$ V.S., 3 mils of ammonioferric sulphate solution, and 5 mils of diluted nitric acid (10 per cent and free from nitrous compounds).

Dilute the liquid with 75 mils of distilled water, and titrate it with the sulphocyanate solution.

At first a white precipitate of silver sulphocyanate is produced, giving the fluid a milky appearance, and then as each drop of sulphocyanate falls in it is surrounded by a deep brownish-red cloud of ferric sulphocyanate, which quickly disappears on shaking, as long as any of the silver nitrate remains unchanged.

When the point of saturation is reached and the silver has all been precipitated, a single drop of the sulphocyanate solution produces a faint brownish-red color, which does not disappear on shaking.

Note the number of mils of the sulphocyanate solution used, and dilute the whole of the remaining solution so that equal volumes of this and of the decinormal silver nitrate will be required to produce the permanent brownish-red tint. (The same tint of brown or red to which the volumetric solution is adjusted must be attained when the solution is used in volumetric testing.)

Assuming that 19 mils of the sulphocyanate solution were

required to produce the reaction, then each 19 mils must be diluted to make 20 mils, or the whole of the remaining solution in the same proportion.

Always make a new trial after the dilution to see if the solutions correspond, e.g., 50 mils of $\frac{N}{10}$ silver nitrate are taken, and 5 mils of ammonioferric sulphate, 5 mils of pure nitric acid and 200 mils of water are added, and there should be required exactly 50 mils of the potassium sulphocyanate solution. The same depth of reddish-brown tint should be obtained in all assays by this method, as is obtained in standardizing the solution.

Estimation of Soluble Haloid Salts

The estimation of these salts is based upon the powerful affinity existing between the halogens and silver, and the ready precipitation of the resulting chlorid, bromid and iodid. Standard solution of silver nitrate is used for this purpose, and for the sake of exactness and convenience, is made of decinormal strength. In some cases it is advisable to use centinormal solutions.

Mohr's Method with Chromate Indicator. This method is the best to use, if the haloid salts are in neutral solution, and salts of lead, bismuth, barium or iron are absent. If the solution is acid the indicator is inadmissable, in that acids have a solvent action upon silver chromate and thus prevent the end-reaction from being clearly and accurately observed. If the above-mentioned metals are present, the indicator is likewise useless, as these bases form insoluble, highly colored compounds with the chromate. The neutral potassium chromate (yellow chromate) which is used as the indicator must be

free from chlorid * and should be used in the form of a 10 per cent solution.

In the volumetric analysis of soluble haloid salts (chlorids, bromids and iodids) 0.5 gm. of the well-dried salt is dissolved in 40 mils of water in a beaker. This is placed upon a white surface and a few drops of the chromate indicator (or sufficient to give the solution a pale yellow tint), added. The decinormal $\frac{N}{10}$ silver nitrate solution is then added cautiously from a burette, stirring constantly until a permanent red tint is produced. The red tint is due to the formation of silver chromate, which does not appear permanent until the last trace of halogen has been precipitated.

The reactions are as follows:

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

and

$$K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3.$$

If the solution to be estimated is acid it should be accurately neutralized with ammonia, or sodium or calcium carbonate. If it is alkaline in reaction it should likewise be neutralized, using acetic acid for this purpose.

In the estimation of bromids and iodids it must not be forgotten to take into account the invariable presence of chlorids as an impurity.

The method in detail is exemplified in the following assay:

Estimation of Sodium Chlorid. One gm. of the well-dried sodium chlorid is dissolved in sufficient distilled water to measure 100 mils. Of this solution 10 mils (representing 0.1

* The presence of chlorid in the chromate solution may be determined by adding a small quantity of silver nitrate solution, and then some nitric acid. If the red precipitate dissolves completely and leaves a clear solution chlorid is absent. If it is found to be present it may be removed addition of a few drops of silver nitrate solution, and filtering, wit any nitric acid.

ced would, f the end-

gm. of the salt) is taken, a few drops of neutral potassium chromate solution added, and then the $\frac{N}{10}$ silver solution delivered from a burette with constant stirring or shaking until the chlorid is entirely precipitated, as evidenced by the formation of a permanent red color (silver chromate). The equation is

$$\underset{10)58.46}{NaCl} + \underset{10)169.89}{AgNO_3} = AgCl + NaNO_3.$$
$$\underset{5.846}{} \qquad \underset{16.989 \text{ gms.} = 1000 \text{ mils } \frac{N}{10} \text{ V.S.}}{}$$

Thus each mil of $\frac{N}{10}$ V.S. represents 0.005846 gm. of NaCl. If in the above assay 17 mils of the silver solution were required, then 17×0.005846 gm. $= 0.099382$ gm. or 99.382 per cent.

$$\frac{0.099382 \times 100}{0.1} = 99.382 \text{ per cent.}$$

Titration without an Indicator—Gay-Lussac's Method. In this method no indicator is used, the standard solution being added until it ceases to produce any further precipitation. This method is applicable to acid solution of the haloid salts, and to the haloid acids—hydrochloric, hydrobromic and hydriodic; also to the estimation of silver by standard solution of sodium chlorid. The method is carried out in hot solutions, slightly acidulated with nitric acid, in order to facilitate the precipitation of the silver halid. The haloid acids are neutralized with an alkali and then *slightly* acidulated with nitric acid before the titration is begun. The calculations are precisely like those in the foregoing assays.

Volhard's or Sulphocyanate Method. This method depends on completely precipitating the halogen in the presence of nitric acid, by a measured excess of standard silver nitrate solution, and then estimating the excess of silver by retitrating

with standard sulphocyanate solution, using ferric alum as an indicator.

The sulphocyanate has a greater affinity for silver than it has for iron, and therefore, so long as any silver is in solution, the sulphocyanate will combine with it and form a precipitate of silver sulphocyanate.

As soon as the silver is all taken up, the sulphocyanate will combine with the ferric alum and strike a brownish-red color.

The sulphocyanate solution is to be made of such strength that it corresponds with the silver solution, volume for volume.

The difference between the volume of silver solution originally added and the volume of sulphocyanate solution used, will give the volume of silver solution equivalent to the haloid salt present.

This method has the advantage over the direct method for haloids with chromate indicator, in that it may be used in the presence of nitric acid. It thus enables one to estimate the haloids in the presence of phosphates or other salts which precipitate silver in neutral but not in acid solutions, and also in that the presence of barium, bismuth, lead, iron and other metals do not interfere, as they do with the chromate in Mohr's method. The presence of mercury, however, exerts a disturbing influence upon the end-reaction. The nitric acid acidulates the solution and thus facilitates the precipitation of silver by the halogens, and prevents its precipitation by other substances. The quantity of nitric acid employed is of no great importance, except in the case of iodids (because silver iodid is slightly soluble in nitric acid). Usually sufficient of the acid is added to just remove the color produced by the indicator. A very large excess of the acid would, however, interfere with the proper determination of the end-

reaction, in that it to a slight extent prevents the formation of ferric sulphocyanate. In the estimation of iodids by this method, the nitric acid should be added after the standard silver solution, while in the case of the other haloid salts the acid may be added before.

The indicator also should be added after the standard silver solution, when estimating iodids, because being a ferric salt it is, like nitric acid, capable of liberating iodin.

The solutions required for this method are:

(I) **Decinormal Silver Nitrate** (page 114);

(II) **Decinormal Potassium Sulphocyanate** (page 117);

(III) **Ferric Alum Solution.** (The indicator.)

This is a 10 per cent aqueous solution of ferric-ammonium sulphate, $FeNH_4(SO_4)_2+12H_2O$.

(IV) **Nitric Acid** (C.P.). This must be free from nitrous acid. If it or any of the lower oxids of nitrogen are present they may be removed by diluting with one-fourth part of water and boiling until colorless.

The process is exemplified in the following assays:

Estimation of Potassium Bromid. Dissolve about 0.4 gm. of the salt accurately weighed in 25 mils of distilled water in a glass-stoppered flask. Add 50 mils of tenth-normal silver nitrate V.S., then add 2 mils of ammonio-ferric sulphate T.S. and 2 mils of nirtic acid, shake well and finally determine the excess of the silver nitrate V.S. by titrating with tenth-normal potassium sulphocyanate V.S. until a permanent reddish tint pervades the supernatant liquid.

The difference between the number of mils of tenth-normal silver nitrate V.S. added and the number of mils of tenth-normal potassium sulphocyanate used, multiplied by 0.011902 gm., gives the weight of pure KBr in the quantity of salt taken for analysis.

Assuming that in the foregoing analysis 16.9 mils of the sulphocyanate solution were used, then $50-16.9=33.1$ mils of the silver nitrate solution reacted with the potassium bromid. Hence $0.011902\times 33.1=0.3939$ gm. of KBr, or 98.5 per cent. The reactions are

$$KBr+AgNO_3=AgBr+KNO_3.$$

$$10000)119.02$$

$$.011902 \text{ gm.} = 1 \text{ mil of } \frac{N}{10} AgNO_3 \text{ V.S.}$$

Iodids are estimated in exactly the same manner.

When this method is used for the estimation of chlorids, however, the precipitated silver chlorid must be removed by filtration, because of the action of ferric sulphocyanate upon silver chlorid, which causes the results of the analysis to be too high.

In the case of silver bromid or iodid no such reaction takes place, or if it does, the reaction is so slow as not to interfere in the least with the getting of accurate results. Therefore, when this method is used for the determination of bromids or iodids, there is no need for filtering to remove the precipitate.

The procedure in detail is exemplified by the following:

Estimation of Sodium Chlorid. Dissolve about 0.2 gm. of the salt accurately weighed (or a near equivalent of its solution) in 25 mils of distilled water in a 200-mil graduated flask. Add 50 mils of tenth-normal silver nitrate V.S. to the solution, and after adding 5 mils of nitric acid, add sufficient distilled water to make 200 mils and mix well. Then filter through a dry filter into a dry flask, and reject the first 20 mils of the filtrate. Collect the next 100 mils of filtrate, add 2 mils of ammonio-ferric sulphate T.S. and titrate it with tenth-normal potassium sulphocyanate until a permanent reddish supernatant liquid is obtained. Multiply the number of

mils of the potassium sulphocyanate solution required by 2 and subtract this figure from 50 (the number of mils of tenth-normal silver nitrate V.S. added). The difference multiplied by the decinormal factor of sodium chlorid, 0.005046 gm., gives the weight of pure NaCl in the amount of salt taken for analysis.

Estimation of Haloid Acids

These acids, namely, hydrochloric, hydrobromic and hydriodic, may be estimated by **Gay-Lussac's** method above described, or they may be estimated by **Mohr's Method.** using neutral potassium chromate as an indicator. In this case it is necessary to carefully neutralize the acid with ammonia and then titrate with $\frac{N}{10}$ silver nitrate solution, using a few drops of chromate as indicator, in the manner described in the foregoing assays. They may also be estimated by **Volhard's Method,** in which an excess of the standard silver nitrate solution is used, in the presence of nitric acid, and the amount of the excess determined by residual titration with potassium sulphocyanate, using ferric alum as the indicator. This method is especially useful for iodids and hydriodic acid, in that the nitric acid need not be added until after an excess of silver nitrate solution is used, and thus liberation of iodin by the nitric acid avoided.

The estimation of the haloid acids may also be effected by neutralization with standard alkali, in the same way as other acids, but since hydrobromic and hydriodic acids are now frequently prepared by the method of Fothergill, in which potassium bromid or potassium iodid (according to the acid to be made) is brought in contact with tartaric acid (as shown in the equation), an excess of the latter acid is

unavoidably present, and hence the neutralization method is inapplicable.

$$\underset{\text{Potassium Iodid}}{KI} + \underset{\text{Tartaric acid}}{H_2C_4H_4O_6} = \underset{\text{Potassium Bitartrate}}{KHC_4H_4O_6} + \underset{\text{Hydriodic Acid}}{HI}$$

$$KBr \quad " \quad " \quad HBr$$

Assay of Hydrobromic Acid, Using Chromate as Indicator. Ten gms. of hydrobromic acid are diluted with sufficient distilled water to make 100 mils. Ten mils of this solution, representing 1 gm. of the acid, is exactly neutralized with diluted ammonia water (using litmus solution as indicator); 3 drops of neutral potassium chromate solution are added, and then the $\frac{N}{10}$ silver nitrate run in from a burette until the solution acquires a permanent red tint. The following equation is then applied:

$$\underset{\substack{10)80.92 \\ 8.092 \text{ gms.} = 1000 \text{ mils } \frac{N}{10} \text{ V.S.}}}{HBr} + AgNO_3 = AgBr + HNO_3.$$

If the assay is to be made by the direct percentage method, 8.09 mils of the solution (10 gms. in 100 mils) (representing 0.809 gms. of the acid) should be taken, in which case each mil of the standard silver solution consumed will at once indicate 1 per cent.

Hydriodic and hydrochloric acids may also be assayed by this method.

Assay of Hydriodic Acid by the Sulphocyanate Method. Introduce into a 200-mil stoppered flask 2 gms. of the acid, add 50 mils of distilled water and 25 mils (accurately measured) of decinormal silver nitrate, shake thoroughly, and then add 3 mils of nitric acid, and heat on a water-bath until the pre-

cipitate has a bright yellow color. Then cool and add 2 mils of the ammonio-ferric sulphate T.S., and finally the decinormal potassium sulphocyanate run in slowly from a burette, until a permanent reddish-brown tint is produced. Note the number of mils of sulphocyanate solution employed.

Deduct this from the 25 mils of silver solution added, and multiply the remainder by the factor for HI, which is 0.012793.

I. $$\underset{10)127.93}{HI} + \underset{10)169.89}{AgNO_3} = AgI + HNO_3.$$

12.793 gms. 16.989 gms. = 1000 mils $\frac{N}{10}$ V.S.

0.012793 gm. of HI = 1 mil $\frac{N}{10}$ V.S.

II. $$AgNO_3 + KSCN = AgSCN + KNO_3.$$

III. $$2FeNH_4(SO_4)_2 + 6KSCN = 2Fe(SCN)_3 + (NH_4)_2SO_4 + 3K_2SO_4.$$

The reddish-brown color which marks the end-reaction is due to the formation of $Fe(SCN)_3$ ferric sulphocyanate.

Assuming that in the above titration 10.2 mils of decinormal sulphocyanate were employed, then 25 mils $-$ 10.2 = 14.8 mils.

$$0.012793 \times 14.8 = 0.1893 \text{ gm.}$$

$$\frac{0.1893 \times 100}{2} = 9.46 \text{ per cent.}$$

Assay of Syrup of Hydriodic Acid. Twenty-five mils of the syrup are introduced into a stoppered flask, 100 mils of distilled water are added, followed by 40 mils of decinormal silver nitrate and the mixture thoroughly shaken. Five mils of diluted nitric acid and 3 mils of the ferric alum solution are now added, and after again shaking the mixture it is titrated with decinormal potassium sulphocyanate until a permanent reddish-brown tint appears.

OTHER ASSAYS BY VOLHARD'S METHOD

Assay of Syrup of Ferrous Iodid U.S.P. Dilute about 10 gms. of the syrup, accurately weighed, with 30 mils of distilled water, add 50 mils of tenth-normal silver nitrate V.S. and 5 mils of nitric acid and heat on a water-bath until the precipitate of silver iodid is yellow. Cool, add 2 mils of ferric ammonium sulphate T.S. and determine the residual silver nitrate by titration with tenth-normal potassium sulphocyanate V.S. A permanent reddish-brown tint marks the end point. Not less than 16 mils nor more than 19.3 mils of the latter should be required.

The quantity of tenth-normal sulphocyanate so used deducted from 50 mils (the quantity of tenth-normal silver nitrate V.S. taken in the assay) gives the quantity of the latter (in mils) which reacted with the ferrous iodid.

Each mil of tenth-normal silver nitrate V.S. corresponds to 0.015484 gm. of FeI_2.

$$FeI_2 + 2AgNO_3 = 2AgI + Fe(NO_3)_2.$$

$$\begin{array}{r} 2)309.68 \\ 10)154.84 \\ \hline 15.484 \end{array}$$

15.484 gms. = 1000 mils $\frac{N}{10}$ $AgNO_3$ V.S.

Assuming that in the foregoing assay 16 mils of the tenth-normal sulphocyanate were used, then 50 mils − 16 mils = 34 mils.

$$0.015484 \times 34 = 0.520456 \text{ gm.}$$

$$\frac{0.520456 \times 100}{10} = 5.20 \text{ per cent.}$$

Assay of Phosphoric Acid U.S.P. The neutralization method for the assay of phosphoric acid has been discarded in the U.S.P. IX, and the precipitation with standard silver nitrate is recommended. An excess of the latter solution is added to

the neutralized phosphoric acid, and the residual silver solution determined by titration with standard sulphocyanate.

The procedure is as follows: An accurately weighed quantity of the acid (about 0.1 gm.) is diluted with 10 mils of distilled water, in a 100-mil flask. One drop of phenolphthalein T.S. is added, and the solution carefully neutralized with special potassium hydroxid solution, i.e., one free from chlorid.

Fifty mils of tenth-normal silver nitrate V.S. are now added, the mixture agitated and zinc oxid (free from chlorid) gradually added in small portions at a time, until the liquid is neutral to litmus paper. It is then diluted with sufficient distilled water to measure 100 mils, again thoroughly agitated and filtered through a dry filter, collecting 50 mils of filtrate. To this 50 mils of filtrate is added 2 mils of nitric acid and 2 mils of ammonio-ferric sulphate T.S. and then titrated with tenth-normal potassium sulphocyanate V.S. to the production of a permanent red color.

The number of mils of the latter multiplied by 2 is subtracted from 50 mils (the quantity of tenth-normal silver nitrate V.S. added) and the difference is the quantity of the latter which reacted with the phosphoric acid.

Each mil of tenth-normal silver nitrate V.S. represents 0.0032687 gm. of H_3PO_4.

Notes. The neutralization of phosphoric acid by potassium hydroxid in the presence of phenolphthalein is represented by the equation

$$H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O.$$

An excess of KOH must be avoided, as this reacts with silver nitrate.

The reaction between silver nitrate and the dipotassic phosphate is usually represented by the following equation,

which, for the purposes of this assay, may be considered sufficiently accurate:

$$K_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2KNO_3 + HNO_3.$$

Normal silver phosphate being precipitated.

It is very probable that the supernatant liquid in this reaction contains also some free phosphoric acid, but that seems to be immaterial.

$$3K_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 6KNO_3 + H_3PO_4.$$

The zinc oxid is added in this assay for the purpose of neutralizing the acid or acids liberated in the interaction. This is necessary because silver phosphate (Ag_3PO_4) is soluble in dilute nitric and phosphoric acids. Too large an excess of zinc oxid must be avoided, as it acts upon silver nitrate, precipitating Ag_2O if left in contact too long. It is advisable for this reason to filter as soon as possible after the addition of zinc oxid.

If, as is claimed,* that phosphoric acid is liberated by the interaction of dipotassic phosphate and silver nitrate, the zinc oxid will form with it, zinc phosphate which in a neutral solution is transposed by the silver nitrate into silver phosphate, and zinc nitrate, thus converting all of the phosphoric acid into Ag_3PO_4.

Zinc oxid appears to be the most suitable substance available for this neutralization, because its action upon silver nitrate is very slow and insignificant, if not in large excess.

Assay of Sodium Phosphate. This may be performed by the same method.

Into a 100-mil graduated flask, introduce an accurately-weighed quantity of the salt (about 0.4 gm.), dissolve it in

* J. Rasin, J. A. C. S., Vol. 33, page 1103.

10 mils of distilled water, add 50 mils of tenth-normal silver nitrate V.S. and shake well. Then add gradually pure zinc oxid in small portions, until the liquid is neutral to litmus. Dilute the mixture with distilled water to make 100 mils. Shake thoroughly and filter through a dry filter. Reject the first 20 mils of filtrate. Collect 50 mils, add to it 2 mils of nitric acid and 2 mils of ammonio-ferric sulphate T.S. and titrate with tenth-normal potassium sulphocyanate V.S. to the production of a permanent red color.

Each mil of tenth-normal silver nitrate V.S. used corresponds to 0.004735 gm. of Na_2HPO_4. The calculations are as given in preceding assay.

Assay of Hypophosphites. This is performed by the method just described for phosphoric acid and sodium phosphate. The hypophosphites being first oxidized to phosphates. Dissolve about 1 gm. (accurately weighed) of the salt in 10 mils of distilled water and 10 mils of nitric acid and evaporate the solution to dryness, on a water-bath. Then add 5 mils of nitric acid and again evaporate it to dryness on a water-bath. Dissolve the residue in 20 mils of distilled water, add a drop of phenolphthalein T.S., and sufficient *special potassium hydroxid* T.S. (free from chlorids) to produce a pale pink color, and then dilute the mixture to exactly 100 mils, with distilled water. Transfer 10 mils of this solution to a 100-mil flask, add 50 mils of tenth-normal silver nitrate V.S. and proceed from this point as directed under assay of sodium phosphate.

Each mil of tenth-normal silver nitrate V.S. corresponds to

0.002836 gm. of $Ca(PH_2O_2)_2$;

0.003472 gm. of KPH_2O_2;

0.0035357 gm. of $NaPH_2O_2$.

Estimation of Cyanogen

Titration with Standard Silver Solution to First Appearance of a Precipitate—Liebig's Method. This gives fairly accurate results. The cyanogen must be in the form of an alkali salt and in an alkaline solution. If hydrocyanic acid is to be estimated, it must be made alkaline by the addition of potassium or sodium hydroxid. The standard silver solution is then added cautiously and with constant stirring until a permanent precipitate of silver cyanid is produced. When silver nitrate is added to an alkaline solution of a cyanid, the precipitate which at first forms redissolves on stirring and a soluble double cyanid (AgCN,KCN or AgCN,NaCN, depending upon the alkali used) is formed, and when all of the cyanid has been taken up, the further addition of silver nitrate causes a decomposition of this soluble double salt and the formation of a permanent precipitate of silver cyanid. Therefore, the first appearance of this precipitate affords a delicate proof of the completion of the reaction.

These equations illustrate the reactions:

$$2NaCN + AgNO_3 = \underset{\text{Double cyanid of silver and sodium}}{AgCN,NaCN} + NaNO_3.$$

$$AgCN,NaCN + AgNO_3 = 2\underset{\text{Silver cyanid}}{AgCN} + NaNO_3.$$

According to these equations it is seen that the end-reaction is reached when two molecules of the alkali cyanid have reacted with one molecule of silver nitrate. The slightest excess of silver nitrate above this quantity brings about a decomposition of the double salt and a precipitation of the silver cyanid, as above stated.

This double combination is so firm that if the estimation is done in the presence of a halogen, no permanent precipitate

of silver halid is formed until after all of the cyanogen present has been converted into a double salt. This fact is taken advantage of in the processes for hydrocyanic acid and alkali cyanid in which potassium iodid is employed as indicator in the presence of ammonia water. The latter prevents the precipitation of silver cyanids and thus allows the silver iodid to precipitate alone.

$$1 \text{ mil of } \frac{N}{10} AgNO_3 \text{ V.S.} = \begin{cases} 0.005204 \text{ gm. CN;} \\ 0.005404 \text{ gm. HCN;} \\ 0.0098 \text{ gm. NaCN;} \\ 0.0130 \text{ gm. KCN.} \end{cases}$$

Titration with Standard Silver Solution, Using Chromate Indicator—Vielhaber's Method. This method is especially recommended for the assay of weak solutions containing hydrocyanic acid, as bitter almond oil, bitter almond water, cherry laurel water, etc., but it may also be employed for alkaline cyanids.

A sufficient quantity of an aqueous suspension of magnesium hydroxid * to make the solution opaque and distinctly alkaline is added; this is followed by a few drops of potassium chromate indicator and then the $\frac{N}{10}$ silver nitrate delivered into the mixture from a burette until a permanent red tint appears, as in the titration of haloid salts. The method is a very satisfactory one if chlorids are absent.

The reactions in this method are the same as in the foregoing, but the end-reaction (the production of silver chromate) does not occur until the double cyanid is completely decom-

* Calcined magnesia triturated with water.

posed, at which point the addition of another drop of silver solution reacts with the chromate and produces the red precipitate (silver chromate).

The equations are as follows: Sodium is used in the equations instead of magnesium in order to make the explanation clearer.

(*a*) $2NaCN + AgNO_3 = AgCN,NaCN + NaNO_3 = (2HCN)$;

(*b*) $AgCN,NaCN + AgNO_3 = 2AgCN + NaNO_3$.

These equations show that it requires two molecules of silver nitrate to completely precipitate two molecules of cyanid. 169.89 gms. of $AgNO_3$ is equivalent to 27.01 gms. of HCN, while by Liebig's method 169.89 gms. of $AgNO_3$ is equivalent to 54.02 gms. of HCN.

$$1 \text{ mil } \frac{N}{10} AgNO_3 \text{ V.S.} = \begin{cases} 0.002602 \text{ gm. CN;} \\ 0.002702 \text{ gm. HCN;} \\ 0.004902 \text{ gm. NaCN;} \\ 0.006511 \text{ gm. KCN.} \end{cases}$$

Example. 1.35 gms. of the diluted acid is mixed with enough water and magnesia to make an opaque mixture of about 10 mils. Add to this 2 or 3 drops of potassium chromate solution and then from a burette deliver the decinormal silver nitrate V.S. until a red tint is produced which does not disappear by shaking.

This method is exemplified in the U.S.P. IX *Assay of Oil of Bitter Almonds.*

Titration with Standard Silver Solution, Using Potassium Iodid as Indicator. This method, employed in the *Assay of Dilute Hydrocyanic Acid*, U.S.P. IX, is conducted as follows:

Into a 100-mil flask containing 25 mils of distilled water and 5 mils of potassium hydroxid T.S., which has been tared,

pour about 5 mils of the acid, and weigh it accurately. Then add 3 drops of potassium iodid T.S. and titrate with tenth-normal silver nitrate V.S. to the production of a slight permanent precipitate.

Each mil of tenth-normal silver nitrate V.S. used, corresponds to 0.005404 gm. of HCN. The slight precipitate which is produced in this assay and which marks the end reaction, is silver iodid (AgI).

The precipitate of silver iodid does not appear until the cyanid has been entirely converted into the double salt (AgCN.KCN).

Estimation of Potassium Cyanid (KCN = 65.11). One gm. of potassium cyanid is dissolved in sufficient distilled water to make 100 mils, then 65.11 mils of this solution mixed with 5 mils of ammonia water and 3 drops of potassium iodid solution are titrated with $\frac{N}{10}$ $AgNO_3$ V.S. until the appearance of a permanent precipitate. Each mil indicates 2 per cent.

$$1 \text{ mil of } \frac{N}{10} AgNO_3 \text{ V.S.} = 0.0130 \text{ gm. KCN.}$$

Estimation of Silver Salts

Soluble silver salts may be estimated by direct titration with standard sodium chlorid, the process being exactly the converse of the precipitation methods for halogens. The standard sodium chlorid solution is added to the solution of the silver salt until precipitation ceases; or the titration may be done in the presence of chromate indicator, the end-point being then known, to be reached when the red color of the silver chromate disappears. The first of these methods is impracticable, too much time being consumed in waiting for the precipitate to settle so as to render the supernatant liquid

sufficiently clear to recognize whether a precipitate is produced in it by the further addition of the standard solution.

If chromate indicator is used, the end-point is easily overstepped, because of the slow decomposition of the silver chromate by the chlorid. It is better to add an excess of sodium chlorid solution and then retitrate with standard silver nitrate solution until the red color appears.

Silver salts may also be titrated by means of standard sulphocyanate solution, using ferric alum as indicator.

Assay of Silver Nitrate by Means of $\frac{N}{10}$ Sulphocyanate. This method, as applied to the assay of halogen compounds, is described in the preceding pages. The great advantage which this method presents over the others, is that the presence of most other metals does not interfere. The only metal which does materially interfere with the determination of silver is mercury.

Example. Weigh accurately about 0.8 gm. of the silver salt, and dissolve it in 50 mils of distilled water, add 2 mils of nitric acid and 2 mils of ferric-ammonium sulphate T.S. and titrate the mixture with tenth-normal potassium sulphocyanate V.S. until a permanent reddish color of ferric sulphocyanate appears.

The following equation explains the reactions:

$$\underset{10)169.89}{AgNO_3} + \underset{10)97.18}{KSCN} = AgSCN + KNO_3.$$

16.989 gms. 9.718 gms. or 1000 mils standard V.S.

Thus each mil of the standard V.S. represents 0.016989 gm. of pure silver nitrate, or 0.010788 gm. of metallic silver.

Assay of Metallic Silver and Silver Alloys. A quantity of the metal, weighing about 0.5 gm., is dissolved in 10 mils of nitric acid, and after complete solution is attained it is

heated sufficiently to drive off all traces of nitrous acid. The solution is then diluted with about 100 mils of distilled water and assayed by one of the methods described under the assay of silver nitrate. The sulphocyanate method is the preferred one.

Assay of Silver Oxid. About 0.5 gm. is dissolved in 3 mils of nitric acid and 50 mils of distilled water, 2 mils of ferric-ammonium sulphate T.S. are added and the mixture titrated with a standard sulphocyanate solution.

Assay of Mercuric Salts by Direct Titration with Sulphocyanate Solution. This method is applicable to most mercuric compounds in the absence of halogens (especially chlorin). It consists in titrating the mercuric salt in the presence of nitric acid and a large volume of distilled water with a standard sulphocyanate solution.

Ferric ammonium sulphate is used as indicator. The assay is carried out as follows:

Assay of Mercuric Oxid. Dissolve an accurately weighed quantity (about 0.5 gm.) of the mercuric oxid in 10 mils of distilled water and 5 mils of nitric acid. Then further dilute the solution with 150 mils of distilled water. To this add 2 mils of ferric-ammonium sulphate T.S. and titrate with tenth-normal potassium sulphocyanate V.S. to the production of a permanent yellowish-red color. Each mil of the sulphocyanate solution used corresponds to 0.01083 gm. of HgO.

$$HgO + 2HNO_3 + 2KCNS = Hg(CNS)_2 + 2KNO_3 + H_2O.$$

This process, while not strictly a precipitation analysis, is for the sake of convenience included under this heading. The mercuric sulphocyanate formed in the process is so sparingly soluble in water that if a high dilution of the salt being titrated is not made, a heavy white precipitate would be produced.

TABLE OF SUBSTANCES ESTIMATED BY PRECIPITATION

Name.	Formula.	Molecular Weight.	Standard Solution Used.	Factor.*
Acid, hydrobromic	HBr	80.93	$\frac{N}{10}$ $AgNO_3$	0.008093
" hydrochloric	HCl	36.47	$\frac{N}{10}$ $AgNO_3$	0.003647
" hydrocyanic	HCN	27.02	$\frac{N}{10}$ $AgNO_3$ without indicator	0.005404
" "	HCN	27.02	$\frac{N}{10}$ $AgNO_3$ with chromate indicator	0.002702
" "	HCN	27.02	$\frac{N}{10}$ $AgNO_3$ with iodid indicator	0.005404
" hydriodic	HI	127.93	$\frac{N}{10}$ $AgNO_3$	0.012793
Allyl-iso-thiocyanate	$CSNC_3H_5$	99.12	"	0.004956
Ammonium bromid	NH_4Br	97.96	"	0.009796
" chlorid	NH_4Cl	53.50	"	0.00535
" iodid	NH_4I	144.96	"	0.014496
Calcium bromid	$CaBr_2$	199.93	"	0.009996
" chlorid	$CaCl_2$	111.01	"	0.00555
Ferrous bromid	$FeBr_2$	215.66	"	0.010784
" iodid	FeI_2	309.66	"	0.015484
Lithium bromid	LiBr	86.86	"	0.008686
Potassium bromid	KBr	119.02	"	0.011902
" chlorid	KCl	74.56	"	0.007456
" cyanid	KCN	65.11	$\frac{N}{10}$ $AgNO_3$ without indicator	0.013022
" "	KCN	65.11	$\frac{N}{10}$ $AgNO_3$ with chromate indicator	0.006511
" "	KCN	65.11	$\frac{N}{10}$ $AgNO_3$ with iodid indicator	0.013022

* This is the coefficient by which the number of cc. used of the decinormal solution is to be multiplied in order to obtain the quantity of pure substance in the sample analyzed. It represents the weight of the substance precipitated by 1 cc. of the decinormal solution.

TABLE OF SUBSTANCES ESTIMATED BY PRECIPITATION—
Continued

Name.	Formula.	Molecular Weight.	Standard Solution Used.	Factor.*
Potassium iodid	KI	166.02	$\frac{N}{10}$ $AgNO_3$	0.016602
" sulphocyanate	KSCN	97.18	"	0.009718
Silver (metallic)	Ag_2	2×107.88	$\frac{N}{10}$ NaCl or $\frac{N}{10}$ KSCN	0.010788
" nitrate	$AgNO_3$	169.89	"	0.016989
" oxid	Ag_2O	231.76	"	0.011588
Sodium bromid	NaBr	102.92	$\frac{N}{10}$ $AgNO_3$	0.010292
" chlorid	NaCl	58.46	"	0.005846
" iodid	NaI	149.92	"	0.014992
Strontium bromid	$SrBr_2$	247.47	"	0.012373
" iodid	SrI_2	341.47	"	0.017573
Zinc bromid	$ZnBr_2$	225.21	"	0.011260
" chlorid	$ZnCl_2$	136.29	"	0.006814
" iodid	ZnI_2	319.21	"	0.015960

CHAPTER X

ANALYSIS BY OXIDATION AND REDUCTION

An extensive series of analyses are made by these methods with extremely accurate results; in fact, the results are generally more accurate than those obtained by gravimetric methods.

The principle involved is exceedingly simple. An oxidizing agent is employed for the estimation of an oxidizable substance, and likewise a reducing agent is employed for the estimation of a reducible substance. Oxidizing agents are always reducible and reducing agents always oxidizable. An oxidation and a reduction take place at the same time, i.e., the oxidizing agent is itself reduced in the operation and the reducing agent is at the same time oxidized.

Thus substances which are capable of absorbing oxygen or are susceptible of an equivalent action may be accurately estimated by subjecting them to the action of an oxidizing agent of known power, and from the quantity of the latter required for complete oxidation the weight of the oxidizable substance is ascertained.

Example. Ferrous oxid (FeO), an oxidizable substance, is ever ready to take up oxygen, while potassium permanganate and potassium dichromate are always ready to give up some of their oxygen. When potassium permanganate gives up its oxygen in this way it is reduced and decolorized, while the ferrous oxid in taking up oxygen is oxidized to ferric oxid (Fe_2O_3). The decolorization of the permanganate here spoken of is taken advantage of in volumetric analysis for the determination of the completion of the oxidation. The permanganate in the form of a standard solution being slowly delivered

from a burette, until it is no longer decolorized, the iron salt is known to be completely oxidized, when the permanganate is no longer reduced. The reaction is as follows:

$$\underset{\text{Ferrous oxid}}{10FeO} + 2KMnO_4 = \underset{\text{Ferric oxid}}{5Fe_2O_3} + 2MnO + K_2O.$$

The oxidation of ferrous oxid by potassium dichromate is shown by the following equation:

$$6FeO + K_2Cr_2O_7 = 3Fe_2O_3 + Cr_2O_3 + K_2O.$$

As before stated, an oxidation is always accompanied by a reduction, the oxidizing agent being itself reduced in the operation. As shown in the above equations, the manganic compound is reduced to a manganous, and the chromic to a chromous, while the ferrous salt is oxidized to a ferric condition.

In the same way any substance which readily yields oxygen in definite quantity or is susceptible of an equivalent action which involves its reduction to a lower quantivalence, may be estimated by ascertaining how much of a reducing agent of known power is required for its complete reduction.

Example. The available chlorin in bleaching powder may be accurately ascertained by treating it with a standard solution of arsenous oxid, and from the volume of the solution required for the complete reduction of the chlorin, the quantity of the latter present is found, or in other words, from the quantity of arsenous oxid (As_2O_3), oxidized to arsenic oxid (As_2O_5) the weight of the chlorin present is ascertained.

The principle substances which are used as oxidizing agents in volumetric analysis, are potassium permanganate, potassium dichromate and iodin. The latter contains no oxygen, but it abstracts hydrogen from accompanying water and liberates the oxygen which does the oxidizing, hence iodin is known as an indirect oxidizing agent. The other two

contain available oxygen which they readily give up when brought in contact with an oxidizable substance.

The principal reducing agents or deoxidizers which are used in volumetric analysis are, sodium thiosulphate, sulphurous acid, oxalic acid, arsenous oxid, stannous chlorid, ferrous oxid, hydriodic acid, hydrosulphuric acid, metallic zinc, and magnesium.

Preparation of Decinormal $\left(\frac{N}{10}\right)$ Potassium Permanganate ($2KMnO_4 = 316.06$; $\frac{N}{10}$ V.S. = 3.1606 gms. in 1 liter). Absolutely pure potassium permanganate cannot be obtained, therefore the preparation of a decinormal solution of this salt cannot be effected by simply dissolving the requisite proportion of the molecular weight in the water. The presence of oxidizable matter in the water used, the contact of dust and exposure to light, have a tendency to decompose the salt and hence weaken the standard solution. It is therefore advisable to use boiling distilled water, and to preserve the solution in amber glass bottles, provided with ground-glass stoppers. It will then retain its strength for several weeks, but should nevertheless be checked by titration immediately before using. It is not necessary, and it is usually undesirable, to make the solution an exact decinormal one. It is preferable to fix the titer of the solution and employ it as it is.

Place 3.5 gms. of pure crystallized potassium permanganate in a flask, add 1000 mils of distilled water, and boil until the crystals are dissolved; put a plug of absorbent cotton in the mouth of the flask and set it aside for two days so that any suspended matter may deposit. After the lapse of this time pour off the clear solution into a glass-stoppered bottle, and when wanted for use standardize by either of the following methods:

Standardization by Means of Iron. Thin annealed binding-wire, free from rust, is one of the purest forms of iron.*

0.1 gm. of such iron is placed in a flask which is provided with a cork through which a piece of glass tubing passes, to the top of which a piece of rubber tubing is attached, which has a vertical slit about one inch long in its side, and which is closed at its upper end by a piece of glass rod (this arrangement is known as the "Bunsen Valve"). (See Fig. 41.) Diluted sulphuric acid is added and gentle heat applied. The iron dissolves and the steam and liberated hydrogen escape through the slit under slight pressure. The air is thus prevented from entering and the ferrous solution protected from oxidation.

A better form of apparatus in which to dissolve the iron and avoid oxidation through admission of air is shown in Fig. 42. A 100-mil flask is fitted with a rubber stopper and a ⌐¬ shaped glass tube; into this flask is placed 20 mils of diluted sulphuric acid (1:5) and then 2 or 3 crystals of

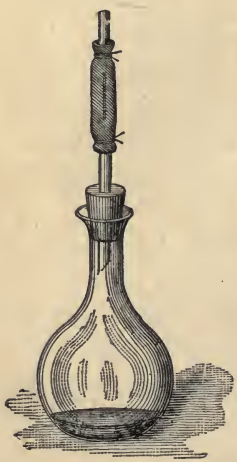

Fig. 41.

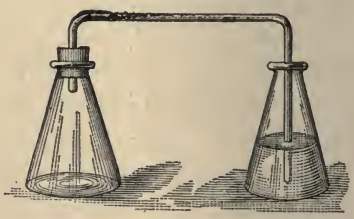

Fig. 42.

pure sodium carbonate; this causes an evolution of carbon dioxid which expels the air from flask. The 0.1 gm. of iron

* This contains 99.6 per cent of iron.

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wire above described is now introduced, the stopper inserted, and a beaker containing a solution of pure sodium carbonate placed in position so that the tube will dip into the solution. Gentle heat is applied until the iron is wholly dissolved, and only a few minute particles of carbon remain (which must not be mistaken for iron). When the flame is withdrawn the cooling of the flask and contents causes a drawing up of the sodium carbonate solution, but the first drops that enter the flask cause an effervescence with evolution of carbon dioxid, which drives the liquid back and at the same time fills the flask with the gas; this is repeated until the flask and contents are cold. Another useful form of apparatus for this purpose is shown in Fig. 43.

Fig. 43.

When the iron is completely dissolved a small quantity of cold, recently boiled, distilled water should be used to rinse the lower end of the stopper and the neck of the flask, and the titration with potassium permanganate at once begun and continued until a faint permanent pink color is produced. If the solution is decinormal, exactly 17.84 mils will be required to produce this result.

The iron is converted by the sulphuric acid into ferrous sulphate, $Fe_2 + 2H_2SO_4 = 2FeSO_4 + 2H_2$. This ferrous sulphate is easily oxidized by the air, and therefore it is directed that access of air should be prevented, and the distilled water with

which the solution is diluted previously boiled in order to drive off any dissolved free oxygen.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4$$

100)558.2 100)316.06

5.582 gms. 3.1606 gms. or 1000 mils $\frac{N}{10}$ V.S.

$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

This equation, etc., shows that each mil of $\frac{N}{10}$ permanganate represents 0.005582 gm. of metallic iron.

Standardization by Means of Oxalic Acid. 0.12605 gm. of the pure crystallized acid is weighed (or 20 mils of decinormal oxalic acid carefully measured) and placed in a flask with 3 mils of sulphuric acid C. P. and distilled water to make 100 mils. The solution is warmed to 85° C. and the permanganate solution delivered in from a burette.

The action is in this case less decisive and rapid than in the titration with iron, and more care should be used. The color disappears slowly at first, but afterwards more rapidly.

Note the number of mils of the permanganate solution used, and then dilute the remainder so that equal volumes of it and of decinormal oxalic acid solution will exactly correspond.

Example. Assuming that 18.5 mils of the permanganate solution are required to produce a permanent pink tint in the above test, then the permanganate solution must be diluted with distilled water in the proportion of 18.5 mils of the permanganate solution and 1.5 mils of water, or 1850 mils to 150 mils.

After dilution a new trial should be made, in which 50 mils of the diluted permanganate solution should require exactly 50 mils of $\frac{N}{10}$ oxalic acid V.S.

The reaction between potassium permanganate and oxalic acid is illustrated by the following equation:

$$2KMnO_4 + 5(H_2C_2O_4 . 2H_2O) + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O.$$

Standardization by the Iodometric Method. This method, which was proposed by Volhard, is the most accurate and rapid for the standardization permanganate. It is based upon the fact that potassium permanganate reacts with potassium iodid in solutions acidulated with either hydrochloric or sulphuric acid, and liberates an equivalent quantity of iodin, which may be estimated by standard solution of sodium thiosulphate. The reactions are illustrated by the equations

(*a*) $$\underset{316.06}{2KMnO_4} + 8H_2SO_4 + 10KI = 2MnSO_4 + 6K_2SO_4 + 8H_2O + \underset{1269.2}{5I_2};$$

(*b*) $$\underset{253.84}{I_2} + 2\underbrace{(Na_2S_2O_3 . 5H_2O)}_{496.44} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

Thus it is seen that $2KMnO_4$ (316.06 gms.) containing five atoms of available oxygen, has the power of liberating its equivalent of iodin, i.e., 10 atoms or 1269.2 gms. (see equation *a*) and that 496.44 gms. of sodium thiosulphate will reduce 253.84 gms. of iodin (see equation *b*). Hence 1000 mils of $\frac{N}{10}$ sodium thiosulphate (containing 25.384 gms.) will reduce, and therefore be equivalent to 12.692 gms. of iodin, which in turn represents 3.1606 gms. of potassium permanganate. Therefore 1 mil of the $\frac{N}{10}$ thiosulphate represents 0.012692 gm. of iodin and 0.0031606 gm. of potassium permanganate, which latter is the quantity of potassium permanganate present in 1 mil of its $\frac{N}{10}$ V.S.

The process is conducted as follows: Into a 200-mil flask place about 0.5 gm. of potassium iodid and 10 mils of diluted sulphuric acid, add to this (slowly from a burette) exactly 10 mils of the permanganate solution to be standardized and dilute the mixture (which is brown in color, because of the liberated iodin) with distilled water to about 150 mils. Then slowly titrate (with constant stirring) with an accurately standardized $\frac{N}{10}$ sodium thiosulphate until the color of the solution is a faint yellow, then add a few drops of starch solution and continue the titration until the color is discharged. Note the number of mils consumed and dilute the permanganate with distilled water so that equal volumes of the two solutions correspond to each other.

Example. If 13 mils of the thiosulphate solution were required, then each 10 mils of the permanganate solution must be diluted to 13 mils.

Standardization with Ferrous Ammonium Sulphate (*Mohr's salt*) ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$). 392.14 gms. of this salt contain 55.82 gms. of iron (3.512 gms. contain 0.5 gm. of iron). 3.512 gms. of the salt are accurately weighed out and dissolved in sufficient recently boiled distilled water to make 250 mils. Fifty mils of this solution containing 0.1 gm. of iron are transferred to a small flask, 10 mils of diluted sulphuric acid added, and then the permanganate solution to be standardized is run in slowly until a faint pinkish tint appears. Whatever number of mils is consumed that number represents 0.1 gm. of iron, and must be diluted to 17.91 mils to make the solution exactly decinormal.

Volumetric Analyses by Means of Potassium Permanganate

When potassium permanganate solution is added to a solution of any readily oxidizable substance strongly acidulated with sulphuric acid, it undergoes reduction, as shown in the

equation below. The molecule ($2KMnO_4$) has eight atoms of oxygen which it gives up in the process of oxidation. These eight atoms of oxygen unite with the replaceable hydrogen of an accompanying acid, liberating an equivalent amount of acidulous radical. Three of these atoms of oxygen liberate sufficient acidulous residual to combine with the potassium and manganese of the permanganate, while the other five atoms are available for direct oxidation.

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O,$$

or, for combination with the hydrogen of more acid, more acidulous residual being set free, to combine with the salt acted upon.

$$2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5(SO_4).$$

$5(SO_4)$ when combined with $10FeSO_4$ forms $Fe_{10}(SO_4)_{15}$ or $5Fe_2(SO_4)_3$, ferric sulphate. Thus it is seen that one molecule of potassium permanganate ($2KMnO_4$) has the power of converting 10 molecules of a ferrous salt to the ferric state.

The equation in full is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3.$$

We have seen that $2KMnO_4$ has 5 atoms of oxygen available for oxidizing purposes, and that each of these will combine with 2 atoms of hydrogen. $2KMnO_4$ is consequently chemically equivalent to 10 atoms of hydrogen, and a normal solution of this salt when used as an oxidizing agent is one that contains in one liter one-tenth of the weight of $2KMnO_4$ expressed in grams, and a decinormal solution, one which contains one-hundredth of this weight.

As before stated, when potassium permanganate is brought

in contact with a ferrous salt or other oxidizable substance, it is decomposed and decolorized. Hence when titrating with a standard solution of this salt it is decolorized so long as an oxidizable substance is present. As soon, however, as the oxidation is completed the standard solution retains its color when added to the substance, and the first appearance of a faint red color is the end-reaction, and the oxidation is known to be completed.

In titrating with potassium permanganate it must be remembered that excess of free acid (preferably sulphuric) should always be present in the solution titrated, in order to keep the resulting manganous and manganic oxids in solution; these, forming a dense brown precipitate, would make it difficult if not quite impossible to recognize the pinkish color of the end-reaction. Sulphuric acid alone, if in large excess, has a reducing effect upon potassium permanganate.

Nitric and hydrochloric acids are prejudicial and should be avoided; they are, however, frequently present in salts which are to be analyzed, and in such event should be removed by converting them into sulphate. By adding a small excess of sulphuric acid and applying heat, until hydrochloric acid or nitrous vapors are no longer evolved, the chlorid or the nitrate is converted into sulphate, and the deleterious effect of their presence overcome. Hydrochloric acid, unless present in very small quantities, and the titration conducted at a low temperature, will vitiate the analysis through its action upon the permanganate whereby chlorin is liberated,* thus

$$KMnO_4 + 8HCl = KCl + MnCl_2 + 4H_2O + 5Cl.$$

* This decomposition of the permanganate by hydrochloric acid is due to the presence of ferric salt, which latter seems to act catalytically, for oxalic acid may be accurately titrated with permanganate even in the presence of hydrochloric acid, no chlorin being given off. Thus the decomposition of the permanganate is not due to the hydrochloric acid alone.

A very convenient way of obviating the irregularities due to the presence of hydrochloric acid is to add a few grams of manganous sulphate * to the solution before titrating it.

Mercuric sulphate ‡ and magnesium sulphate may also be used with satisfactory results.

Potassium permanganate, being so readily decomposed by contact with organic matter, should be protected from such contact. It should never be filtered through paper (glass-wool or guncotton may be used), nor should it be used in a Mohr's burette or in any other apparatus in which it is in contact with rubber or cork. Furthermore, all substances of an oxidizing or reducing nature, aside from that being analyzed, must be excluded from the solution. Among such substances may be mentioned hydriodic acid, sulphureted hydrogen, nitrous acid and the lower oxids of nitrogen, phosphorous and hypophosphorous acids, thiosulphuric, sulphurous, and all the other acids of sulphur except sulphuric, also *ous* salts and the metallic suboxids and peroxids.

Burettes and other apparatus which have been used for

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* Kessler and Zimmermann suggest using 20 mils of a solution of manganous sulphate (200 gms. per liter).

‡ Cady and Ruediger (J. A. C. S., XIX, 575) concluded from the following general principles that it is possible to titrate iron with permanganate in the presence of hydrochloric acid if an excess of mercuric sulphate be added to the solution. Mercuric halids in solution ionize to an extremely slight extent, while the mercuric salts of oxyacids are readily ionized, since compounds of slight ionization always result when their constituent ions meet; mercuric halids are always produced when a mercuric salt of an oxyacid is added to a solution containing halogen ions. Therefore when mercuric sulphate solution and hydrochloric acid are mixed, ionization of both occurs, and the mercuric ions unite with the chlorin ions and produce mercuric chlorid which is only very slightly ionized. In the presence of a large excess of mercuric sulphate, the mercuric ions resulting from its dissociation diminish the ionization of the mercuric chlorid until it is practically nil. Thus no chlorin ions will be present in the solution to induce decomposition of the permanganate.

permanganate, should be emptied and rinsed immediately after use, and any manganic oxid which may be adhering to the glass should be removed by means of hydrochloric acid and boiled water.

Not only oxidizable substances but reducible substances may be estimated by means of potassium permanganate.

In the estimation of oxidizable substances the standard potassium permanganate is added directly to the acidulated solution of the substance being analyzed. The completion of the oxidation being then known by the appearance of a faint pinkish tint. This is the *direct method.*

In the estimation of reducible substances (i.e., oxidizing substances) the *indirect* or *the residual method* is employed.

In this an accurately weighed or measured quantity of the substance is brought together with an excess of a third substance having reducing power, and which is similarly effected by the permanganate and by the substance analyzed. After completion of the reaction the excess of the reducing substance is found by titration with standard permanganate. The difference between the quantity so found and that originally added gives the quantity which reacted with the salt under analysis, and from this the calculation is made.

On the Use of Empirical Permanganate Solutions.

A. If the standardization of the solution is done by means of iron, as described on page 142, 0.1 gm. of iron wire (representing 0.0996 gm. of pure iron) will require 17.84 mils of the permanganate solution if the latter is exactly decinormal. If less than this quantity of solution is used (say 17.5 mils) it indicates that the solution is stronger than decinormal, and may either be diluted so that each 17.5 mils will measure 17.84, or it may be used as it is. This latter is in most cases

preferable. The value of 1 mil of the solution in iron is calculated thus:

17.5 mils. : 1 mil :: 0.0996 gm. : x. x=0.00569 gm.

If a solution of this strength is to be used for the estimation of iron, simple multiplication of the number of mils used by 0.00569 gm. gives the weight of Fe present. If, however, this solution is employed for the titration of other oxidizable substances, the number of mils consumed is multiplied by 0.00569 gm. and then by a fraction in which the numerator represents a quantity of the substance examined, equivalent in grams to an atom of iron in its reaction with permanganate, and the denominator is the atomic weight of iron.

Example. If in a titration we use 40 mils of a permanganate solution, the titer of which has been found to be 1 mil =0.00569 gm., the calculation would be:

in the case of ferrous sulphate ($FeSO_4$, 151.89),

$$40\times 0.00569 \text{ gm.}\times\frac{151.89}{55.82}=0.6192 \text{ gm.};$$

in the case of oxalic acid ($H_2C_2O_4.2H_2O=126.05$),

$$40\times 0.00569 \text{ gm.}\times\frac{63}{55.82}=0.256 \text{ gm.};$$

in the case of hydrogen dioxid ($H_2O_2=34$),

$$40\times 0.00569 \text{ gm.}\times\frac{17}{55.82}=0.0693 \text{ gm.}$$

B. Another way. The solution just mentioned, of which 17.50 mils are consumed in titrating 0.1 gm. of iron wire, is compared with a true decinormal permanganate solution, of which 17.84 mils are consumed in the same reaction. The

strength of the former solution is therefore $\frac{1784}{1750}$ as compared with a decinormal solution.

In titrating with this solution the number of mils consumed are to be multiplied by $\frac{1784}{1750}$ and then by the true decinormal factor for the substance being analyzed.

Example. Forty mils of the solution are consumed.

In the case of ferrous sulphate ($FeSO_4 = 151.89$), the decinormal factor (i.e., the weight of ferrous sulphate represented by 1 mil of a true decinormal solution) is 0.015189 gm.

$$40 \times \frac{1984}{1750} \times 0.015189 \text{ gm.} = 0.6192 \text{ gm.}$$

In the case of oxalic acid ($H_2C_2O_4$, $2H_2O = 126.05$), the decinormal factor is 0.0063 gm.

$$40 \times \frac{1784}{1750} \times 0.0063 \text{ gm.} = 0.256 \text{ gm.}$$

In the case of hydrogen dioxid ($H_2O_2 = 34$), the decinormal factor is 0.001688 gm.

$$40 \times \frac{1784}{1750} \times 0.0017 \text{ gm.} = 0.0693 \text{ gm.}$$

C. If the standardization is done by means of oxalic acid, as described on page 144, in which 10 mils of a strictly decinormal oxalic acid solution are titrated with the permanganate solution which is being standardized, exactly 10 mils of the latter will be consumed if it is of decinormal strength. If in the trial, however, it is found that only 9.6 mils are consumed it indicates that the solution is stronger than decinormal; its strength being expressed by $\frac{100}{96}$. If, on the other hand,

more than 10 mils of the solution are consumed (say 10.4 mils) the solution is below decinormal strength, namely, $\frac{100}{104}$.

In using a solution of the first strength the number of mils of it consumed in any titration is to be multiplied by $\frac{100}{96}$ and then by the decinormal factor for the substance examined. In the case of the weaker solution the number of mils consumed is multiplied by $\frac{100}{104}$ and then by the decinormal factor for the substance being analyzed.

Examples. *Ferrous sulphate* ($FeSO_4 = 151.89$) is titrated with the stronger solution, 40 mils of the latter being consumed.

Then $40 \times \frac{100}{96} \times 0.015189$ gm. $= 0.628$ gm.

Oxalic acid ($H_2C_2O_4 \cdot 2H_2O = 126.05$), 40 mils are consumed.

Then $40 \times \frac{100}{96} \times 0.0063$ gm. $= 0.260$ gm.

Hydrogen dioxid ($H_2O_2 = 34$), 40 mils are consumed.

Then $40 \times \frac{100}{96} \times 0.0017$ gm. $= 0.0703$ gm.

D. If the checking of the permanganate solution is done by the iodometric method (page 145) and it is found that 10 mils of the permanganate requires the use of 13 mils of decinormal thiosulphate solution, the titer of the solution is expressed with reference to decinormal as $\frac{13}{10}$. In using a solution of this strength, the number of mils of it consumed in an analysis is multiplied by $\frac{13}{10}$ and then by the decinormal factor for the substance analyzed.

TYPICAL ANALYSES WITH PERMANGANATE

A. Direct Titrations

a. **Estimation of Ferrous Sulphate** ($FeSO_4+7H_2O=278$). One gm. of ferrous sulphate is dissolved in 25 mils of water and the solution strongly acidulated with sulphuric acid. Decinormal potassium permanganate is then delivered from a burette until a permanent pink tint is obtained, indicating the complete oxidation of the ferrous salt.

The reaction is as follows:

$$(10FeSO_4 + 7H_2O) + 2KMnO_4 + 8H_2SO_4$$

$$100)2780 \qquad 100)316.06$$

$$27.80 \text{ gms.} = 3.1606 \text{ gm.} = 1000 \text{ mils } \frac{N}{10} \text{ V.S.}$$

$$2.780 \text{ gms.} = 100 \text{ mils } \frac{N}{10} \text{ V.S.}$$

$$0.0278 \text{ gm.} = 1 \text{ mil } \frac{N}{10} \text{ V.S.}$$

$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MNSO_4 + 78H_2O.$$

Thus 316.06 gms. of permanganate = 2780 gms. of crystallized ferrous sulphate, which equals 55.82 gms. of metallic iron. One mil of $\frac{N}{10}$ permanganate solution therefore represents 0.0278 gm. of $FeSO_4+7H_2O$ or 0.005582 gm. of Fe.

In the analysis 35 mils of the $\frac{N}{10}$ permanganate were consumed. The 1 gm. taken then contains $35\times0.0278=0.973$ gm. or 97.3 per cent.

If it is desired that each cc. of the permanganate solution should represent a certain percentage of pure salt, a molecular quantity of the salt should be taken for analysis instead of 1 gm. For example, if 2.78 gms. be taken, each mil of the decinormal solution consumed will correspond to 1 per cent, because 2.78 gms. is the weight of crystallized ferrous sul-

phate which can be oxidized by 100 mils of the decinormal solution. If half of this weight be taken, i.e., 1.39 gms., each mil of the permanganate solution compound will represent 2 per cent of pure salt.

Granulated Ferrous Sulphate ($FeSO_4+7H_2O$) is estimated in the same way as the foregoing, and should correspond with it in strength.

Exsiccated (*Dried*) *Ferrous Sulphate.* This salt is tested in the same manner as the other two sulphates. It contains a larger percentage of ferrous sulphate than the other two, having less water of crystallization. Its composition is approximately $FeSO_4+3H_2O$.

$$\underset{\substack{100)1518.9\\ 15.189 \text{ gms.}}}{10FeSO_4} + \underset{\substack{100)316.06\\ 3.1606 \text{ gms. or 1000 mils } \frac{N}{10} \text{ standard solution.}}}{2KMnO_4} + 8H_2SO_4$$

$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Each cc. of the standard solution represents 0.015189 gm. of anhydrous (real) ferrous sulphate.

b. **Estimation of Metallic Iron in Ferrum Reductum.** Ferrum reductum (reduced iron) always contains besides metallic iron a varying quantity of oxid. Therefore, in assaying this preparation a method must be employed which will estimate the iron only, which is present as metallic iron. This may be done by means of a solution of mercuric chlorid which reacts with metallic iron only and not with the oxid.

The method is as follows:

Introduce into a 100-mil flask 1 gm. of reduced iron, previously well triturated. Add 10 gms. of powdered mercuric chlorid and 50 mils of boiling distilled water. Boil for five minutes, shaking it frequently, then fill the flask to the 100-mil mark with recently boiled and cooled distilled water.

$$2HgCl_2+Fe_2=2FeCl_2+2Hg.$$

Let it cool to room temperature and again fill to the mark. Shake well, and after a few minutes filter and collect 20 mils of filtrate. Add to this 20 mils of dilute sulphuric acid, and immediately titrate with tenth-normal potassium permanganate V.S. until a permanent pink color is produced.

Each mil of the permanganate solution represents 0.005582 gm. of metallic iron.

$$\begin{array}{cccccc} 10FeSO_4 & + & 2KMnO_4 & + & 8H_2SO_4 \\ 100)558.2 & & 100)316.06 & & \\ 5.582 \text{ gms.} & = & 3.1606 \text{ gms.} = 1000 \text{ mils } \frac{N}{10} \text{ V.S.} & & \\ 0.005582 \text{ gm.} & = & 0.0031606 \text{ gm.} = 1 \text{ mil } \frac{10}{N} \text{ V.S.} & & \end{array}$$

$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Titration with an Empirical Permanganate Solution. A solution of permanganate, which is found upon standardization to be of a strength in which 1 mil is equivalent to 0.00512 gm. of Fe, is to be used.

Each mil of this solution is equivalent to the following quantities:

$FeSO_4$	0.01393 gm.
$FeSO_4+7H_2O$	0.02549 "
$FeCO_3$	0.01062 "
$FeCl_2$	0.01162 "
Fe	0.00512 "

c. **Estimation of Oxalic Acid and Oxalates with Potassium Permanganate Solution** ($H_2C_2O_4+2H_2O=126.05$; $H_2C_2O_4=90$). The estimation of oxalic acid may be accurately made either by neutralization with a standard alkali or by oxidation with standard permanganate. The latter method is, however, the one to be employed in the case of oxalates.

The oxidimetric estimation of oxalic acid is carried out as follows:

One gm. of the acid (accurately weighed) is dissolved in sufficient water to make 100 mils. Of this solution, 10 mils (representing 0.1 gm. of the acid) is taken for analysis. Two mils of diluted sulphuric acid are added, the solution is heated to between 40° C. and 60° C., and keeping it at about this temperature, is titrated with decinormal potassium permanganate, agitating constantly, until a faint rose tint marks the completion of the reaction.

Each mil of the permanganate solution consumed represents 0.0063 gm. of crystallized oxalic acid.

The reaction is as follows:

$$\underset{\substack{100)630.25\\ 6.30\text{ gms.}=}}{5(H_2C_2O_4+2H_2O)}+\underset{}{3H_2SO_4}+\underset{\substack{100)316.06\\ 3.1606\text{ gms.}=1000\text{ mils }\frac{N^1}{10}\text{ V.S.}}}{2KMnO_4}$$

$$=K_2SO_4+2MnSO_4+18H_2O+10CO_2.$$

Direct Percentage Titration. 0.63 gm. of crystallized oxalic acid is oxidized by 100 mils of $\frac{N}{10}$ permanganate. Therefore if 0.63 gm. of the acid is taken for analysis, each mil of $\frac{N}{10}$ permanganate will represent 1 per cent.

Titrating with an Empirical Solution. If the permanganate is checked with iron, we take into consideration that $2KMnO_4$ will oxidize 10 atoms of iron (558.2 parts), and on the other hand 5 molecules of oxalic acid (630.25 parts). If the titer of the permanganate be found on experiment to be 1 mil = 0.00569, whatever number of mils of this solution is consumed is to be multiplied by 0.00569 and then by $\frac{63}{55.82}$.

Example. 0.3 gm. of oxalic acid requires for oxidation 40 mils of a permanganate solution whose titer is 1 mil = 0.00569 gm. Fe, the calculation is made as follows:

$$40\times 0.00569\text{ gm.}\times\frac{63}{55.82}=0.256\text{ gm.}$$

0.256 gm. is the quantity of pure crystallized oxalic acid present in the 0.3 gm. taken for analysis. This is 85.3 per cent.

$$\frac{0.256 \times 100}{0.3} = 85.3.$$

If the standardization of the permanganate is done by means of a decinormal oxalic acid, or by the iodometric method, the calculation is as described on pages 152–153.

Oxalates are estimated in the same manner; a much larger quantity of sulphuric acid is, however, required. This serves to liberate the oxalic acid from its combination.

The presence of precipitates of sulphates of calcium, barium, or lead does not interfere with the recognition of the end-point.

Each mil of $\frac{N}{10}$ potassium permanganate represents

Oxalic acid anhydrous ($H_2C_2O_4$) ..... 0.0045 gm.
Oxalic acid crystallized ($H_2C_2O_4 + 2H_2O$)...0.0063 "

d. **Estimation of Hydrogen Dioxid and Barium Dioxid with Standard Potassium Permanganate.** Hydrogen dioxid (*Hydrogen peroxid*) ($H_2O_2 = 34$). Hydrogen dioxid and potassium permanganate, though both oxidizing agents, will, when mixed in an acid solution, reduce each other. The reaction which occurs is probably primarily an oxidation of the H_2O_2 to a higher oxid (H_2O_4 (?)) which, however, immediately breaks up with the liberation of oxygen. The method of assaying hydrogen dioxid by means of permanganate is applicable not only to this substance but also to the estimation of barium dioxid and the soluble alkali peroxids. The method is usually carried out by adding the permanganate solution to the dioxid in a solution acidulated with sulphuric acid. Immediate decolorization of the permanganate occurs, as long as any

hydrogen dioxid is present. When the latter has been entirely taken up the permanganate is no longer decolorized and a faint pink tint marks the end-point. In the estimation of the pharmacopœial or commercial dioxid solutions, containing 2 or 3 per cent of H_2O_2, a measured quantity is taken for analysis. The specific gravity of the solution, being nearly that of water, 1 cc. is taken to represent 1 gm. In the case of solutions of hydrogen dioxid of high percentage strength, it is advisable to take a weighed quantity for analysis. If hydrochloric acid is present a small quantity of manganese sulphate should be introduced before titrating.

The assay is conducted as follows:

An accurately weighed quantity (about 2 gms.) of the hydrogen dioxid solution is diluted with 20 mils of distilled water, and acidulated with 20 mils of diluted sulphuric acid and then the $\frac{N}{10}$ permanganate solution run in from a burette, stirring after each addition until a permanent faint pink tint appears. The reaction is as follows:

$$\underset{100)170}{5H_2O_2} + \underset{100)316.06}{2KMnO_4} + 3H_2SO_4$$

1.7 gms. 3.1606 gms. = 1000 mils $\frac{N}{10}$ permanganate V.S.

0.0017 gm. = 1 mil $\frac{N}{10}$ permanganate V.S.

$$= K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Thus each mil of $\frac{N}{10}$ permanganate represents 0.0017 gm. of absolute hydrogen dioxid. Assuming that in the above estimation 35.5 mils of the permanganate solution were required, then the 2 gms. taken for analysis contained 0.0017 gm. $\times$ 35.5, which is 0.06035 gm. of absolute H_2O_2. This corresponds to 3.017 per cent.

The Direct Percentage Method. Ten gms. of the solution is diluted with water to measure 100 mils. Seventeen mils of this diluted solution (containing 1.7 gms. of hydrogen dioxid) is acidulated with sulphuric acid and titrated with decinormal permanganate, as above described. Each mil of the permanganate solution consumed will represent 0.1 per cent by weight of H_2O_2.

Titration with an Empirical Solution. A permanganate solution is on hand which is found upon standardization with iron to be 1 mil = 0.00569 gm. Fe. To use this solution as it is, we take into consideration that $2KMnO_4 = (316.06) = 10$ atoms of Fe (558.2) and also 5 molecules of H_2O_2 (170). 31.606 gms. $KMnO_4$, = 55.82 gms. Fe, = 17 gms. H_2O_2. Whatever number of mils of this permanganate solution is used, multiplied by 0.00569 gm. and then by $\frac{17}{55.82}$, will give the weight of H_2O_2 present in the sample analyzed.

Estimation of Volume Strength. Let us look at the above equation in a different light.

We see that when potassium permanganate and hydrogen dioxid react, 10 atoms of oxygen are liberated.

The permanganate itself when decomposed liberates five atoms of oxygen. Therefore of the above ten atoms only five come from the hydrogen dioxid.

$$5H_2O_2 = 5H_2O + 5O;$$

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

In order to find the factor for volume of available oxygen, see the following equation, etc.:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O + 5O.$$

$$\overset{100)316.06}{3.1606 \text{ gms. or } 1000 \text{ mils } \frac{N}{10} \text{ V.S.}} = \overset{100)80}{0.80 \text{ gm.}}$$

$$1 \text{ mil } \frac{N}{10} \text{ V.S.} = 0.0008 \text{ gm.}$$

Thus it is seen that each mil of $\frac{N}{10}$ potassium permanganate V.S. represents 0.0008 gm. of oxygen. But we require to find the volume of oxygen, not the weight represented by 1 mil of $\frac{N}{10}$ permanganate.

1000 mils of oxygen at 0° C. and 760 mm. pressure, weigh 1.43 gms. Therefore, if 1.43 gms. measure 1000 mils, 0.0008 gm. will measure 0.57 mil.

The factor, then, for volume of oxygen liberated when hydrogen dioxid is titrated with $\frac{N}{10}$ potassium permanganate, is 0.57, and the number of mils of the $\frac{N}{10}$ potassium permanganate consumed in the titration gives the volume of oxygen liberated by the quantity of hydrogen dioxid taken.

Thus if 19 mils of the $\frac{N}{10}$ V.S. were required,

$$0.57 \times 19 = 10.83 \text{ mils of oxygen.}$$

It is convenient to operate upon 1 mil of hydrogen dioxid solution. Then each mil of potassium permanganate V.S. used will represent 0.57 mil of available oxygen and is necessary only to multiply the number of mils by this factor to find the volume of available oxygen.

If any other quantity than 1 mil of dioxid be taken for analysis, it will be necessary after multiplying by 0.57 to divide the result by the quantity of dioxid solution taken, in order to find volume strength.

Hydrogen dioxid solution may also be volumetrically assayed by Kingzett's method, which is described under Iodometry.

The gasometric estimation is also described further on.

Barium Dioxid (*Barium Peroxid*) ($BaO_2 = 169.37$). This substance is assayed by treating it with an acid, and then estimating the liberated hydrogen dioxid, as follows:

Weigh off 2 gms. of the coarse powder, put it in a porcelain capsule, add about 10 mils of ice-cold water, then 7.5 mils of phosphoric acid (85 per cent), and sufficient ice-cold water to make 25 mils. Stir and break up the particles with the end of the stirrer until a clear or nearly clear solution is obtained and all that is soluble is dissolved.

Five mils of this solution (which corresponds to 0.4 gm. of barium dioxid) is measured off for assay.

Drop into this from a burette, with constant stirring, decinormal potassium permanganate until a final drop gives the solution a permanent pink tint.

About 40 mils of the decinormal permanganate should be required to produce this result.

In this process, the first step is the formation of hydrogen dioxid by treating the barium dioxid with phosphoric acid, as illustrated by the following equation:

$$\underset{169.37}{BaO_2} + H_3PO_4 = BaHPO_4 + \underset{34}{H_2O_2}.$$

The hydrogen dioxid is then estimated with decinormal permanganate, as described above.

$$\underset{\substack{100)845.85\\ 8.4585 \text{ gms.}=}}{5(BaO_2)} = \underset{\substack{100)170\\ 1.7 \text{ gms.}}}{5H_2O_2} + \underset{\substack{100)316.06\\ 3.1606=1000 \text{ cc. } \frac{N}{10} \text{ permanganate.}}}{2KMnO_4} + 3H_2SO_4$$

$$= K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Sodium Perborate ($NaBO_3 + 4H_2O = 154.06$). Dissolve an accurately weighed quantity (about 0.25 gm.) of the salt in a mixture of 50 mils of distilled water and 10 mils of diluted sulphuric acid, and titrate the solution with tenth-normal

potassium permanganate V.S. until a final drop gives the solution a permanent pink color.

Each mil of the standard permanganate used corresponds to 0.0008 gm. of available oxygen, which should be present in not less quantity than 9 per cent. The reaction involved is represented by the equation:

$$\underset{154.06}{NaBO_3 \cdot 4H_2O} + H_2SO_4 = NaHSO_4 + B(OH)_3 + H_2O_2 + H_2O.$$

Percarbonates may be assayed in the same manner.

$$Na_2C_2O_6 \cdot H_2O + 2H_2SO_4 = 2NaHSO_4 + 2CO_2 + H_2O_2 + H_2O.$$

B. Residual Titrations

a. Methods in which an Excess of Standard Permanganate is Added and the Excess Determined by Residual Titration with Standard Oxalic Acid.

Estimation of Nitrous Acid and Nitrites. Nitrous acid, when brought in contact with a potassium permanganate solution acidulated with sulphuric acid, is oxidized to nitric acid. Two molecules of $KMnO_4$ reacting with 5 molecules of HNO_2, as the equation shows,

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

In the case of nitrites, as for example sodium nitrite, the oxidation takes place in the same manner, and the process may be applied with equally good results to the salts, as well as to free HNO_2. At ordinary temperatures the oxidation proceeds very slowly, but at a temperature of 40° C. (104° F.) rapid reaction occurs. But because of the volatility of nitrous acid in acidulated solutions of its salts it is impossible to accurately estimate them by direct titration with permanganate at a raised temperature.

It is customary to add the nitrite solution to a measured volume of warm acidulated standard permanganate solution and then to titrate the excess of permanganate with standard oxalic acid solution.

The assay is conducted as follows: To 50 mils $\frac{N}{10}$ potassium permanganate V.S. add 100 mils of distilled water and 5 mils of sulphuric acid. To this solution add by means of a pipette 10 mils of a solution of sodium nitrite (1 gm. in 100 mils). In adding the sodium nitrite solution immerse the tip of the pipette beneath the surface of the permanganate mixture. Warm the liquid to 40° C., allow it to stand for five minutes and then titrate with $\frac{N}{10}$ oxalic acid V.S. until the color of the permanganate solution is just discharged. Subtract the number of mils of the oxalic acid solution used from the number of mils of permanganate solution taken, and multiply the remainder by 0.0034505 gm.

$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4$$
$$5 \times 69.01 = 345.05$$
$$= 5NaNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

Each mil of $\frac{N}{10}$ potassium permanganate V.S. corresponds to 0.0034505 gm. of $NaNO_2$.

The Assay of Hypophosphites may be made by the same method.

An accurately weighed quantity of hypophosphorous acid or its salt is dissolved in water, the solution strongly acidulated with sulphuric acid, and then a measured excess of $\frac{N}{10}$ potassium permanganate solution added. The mixture is boiled for fifteen minutes to hasten and facilitate the oxidation and

then the excess of permanganate solution titrated with $\frac{N}{10}$ oxalic acid V.S.

Example. Three gms. of the acid are diluted with water to make 60 mils. Of this solution 6 mils (representing 0.3 gm. of the acid) are carefully removed with a pipette and introduced into a flask. Three mils of sulphuric acid are added and then 50 mils of $\frac{N}{10}$ potassium permanganate solution, and the mixture boiled for fifteen minutes.

The potassium permanganate, in the presence of sulphuric acid, oxidizes the hypophosphorous acid to phosphoric, as the equation shows:

$$\underset{\substack{2)330.2\\100)165.1\\1.651\text{ gms.}}}{5HPH_2O_2} + 6H_2SO_4 + \underset{\substack{2)632.12\\100)316.06\\3.16c6\text{ gms. or 1000 mils }\frac{N}{10}\text{ V.S.}}}{2(2KMnO_4)} = 5H_3PO_4 + 6H_2O + 2K_2SO_4 + 4MnSO_4.$$

Each mil of the decinormal V.S. represents 0.001651 gm. of absolute hypophosphorous acid. The quantity of permanganate solution directed to be added is slightly in excess. The excess is then ascertained by retitration with decinormal oxalic acid. Each mil of oxalic acid required corresponds to 1 mil of decinormal permanganate which has been added in excess of the quantity actually required for the oxidation.

The excess of permanganate colors the solution red, and the oxalic acid V.S. is then added until the red color just disappears, which indicates that the excess of permanganate is decomposed.

If 4.7 mils of decinormal oxalic acid are required, it indicates that 50 mils $-$ 4.7 mils $=$ 45.3 mils of decinormal perman-

ganate were actually used up in oxidizing the hypophosphorous acid; therefore

$$0.001651 \text{ gm.} \times 45.3 = 0.0747 + \text{ gm.}$$

of absolute hypophosphorous acid, HPH_2O_2, or

$$\frac{0.0747 \times 100}{.3} = 24.7 \text{ per cent.}$$

In this process boiling facilitates the oxidation, but if the acid is boiled before sufficient permanganate has been added to completely oxidize it, decomposition will take place. Hence direct titration with permanganate is impossible and the residual method must be resorted to.

b. Methods Involving a Precipitation by Oxalic Acid and the Titration of the Excess of the Latter with Standard Permanganate.

Assay of Calcium Carbonate and Soluble Calcium Salts. Dissolve an accurately weighed quantity of calcium carbonate (0.3 to 0.4 gm.) in 10 mils of distilled water and 10 mils of diluted hydrochloric acid, and boil the solution to expel all carbon dioxid. Transfer this solution to a 200-mil graduated flask, add 100 mils of $\frac{N}{10}$ oxalic acid V.S., render it alkaline with ammonia water, shake well and allow it to stand for three hours at from 60° to 70° C. or overnight at room temperature. Cool the mixture, if necessary dilute with distilled water to the 200-mil mark, mix it well, filter through a dry filter into a dry flask, reject the first 20 mils of filtrate, and proceed as follows: To 100 mils of the filtrate (representing half of the calcium carbonate taken) add diluted sulphuric acid until of acid reaction, then add 25 mils more of the same acid, warm the solution to 60° or 70° C., and titrate with $\frac{N}{10}$ potassium per-

manganate V.S. until a permanent pale pink color is obtained.

Deduct the number of mils of the permanganate solution used (say 10.8 mils) from half the volume of the oxalic acid solution taken (50 mils) and multiply the remainder (39.2 mils) by 0.005 gm. This gives the weight of $CaCO_3$ in half the quantity of the salt taken for analysis.

$$50 - 10.8 = 39.2 \text{ mils};$$

$$39.2 \times 0.005 \text{ gm.} = 0.1960 \text{ gm.};$$

$$\frac{0.1960 \times 100}{.2} = 98 \text{ per cent.}$$

Calcium Oxid (Calx), $CaO = 5607$, is assayed in the same manner.

Estimation of Soluble Calcium Salts. To a weighed quantity of the calcium salt dissolved in water, a measured excess of normal oxalic acid is added. The mixture is then made alkaline with ammonia and boiled, to facilitate the separation of the precipitate. It is then cooled and diluted with water to an accurately measured volume, and after filtration an aliquot portion removed, acidulated with sulphuric acid, and carefully titrated with $\frac{N}{10}$ potassium permanganate.

Example. 0.4 gm. of calcium chlorid is dissolved in water, 10 mils of normal oxalic acid added, the mixture made alkaline with ammonia water, and boiled for a few minutes. It is then filtered, the residue and filter washed with water, and after cooling the combined filtrate and washings are diluted to make 100 mils.

Of this solution 50 mils are taken for analysis (representing 0.2 gm. of the salt), acidulated with sulphuric acid, and then titrated with $\frac{N}{10}$ potassium permanganate to a faint rose tint.

The 50 mils of solution represent 5 mils of normal oxalic acid, which is equivalent to 50 mils of decinormal oxalic acid, so that whatever number of mils of decinormal permanganate solution is required in the titration, that quantity is to be deducted from 50 mils and the difference multiplied by the $\frac{N}{10}$ factor for calcium chlorid to find the quantity of pure $CaCl_2$ present in 0.2 gm.

If 14 mils of $\frac{N}{10}$ permanganate are employed, then 14 from 50 mils leaves 36 mils, the quantity of decinormal oxalic acid solution which combined with the 0.2 gm. of calcium chlorid. Then

$$0.00555 \text{ gm.} \times 36 = 0.1998 \text{ gm.},$$

the quantity of pure $CaCl_2$ present in the 0.2 gm., or 99.9 per cent.

Calcium salts to be estimated by this method must be tolerably pure, and free at least from impurities which would react with oxalic acid or which would reduce permanganate.

Many of the less soluble calcium salts may be estimated by this method, but they must be subjected to longer treatment with the oxalic acid.

Gold and lead salts may also be estimated by the same method.

Estimation of Lead in the Acetate and Subacetate. Take for assay 0.2 gm. of the salt or 2 gms. of the solution in a beaker and add 20 mils of recently boiled distilled water. Pour this slowly and with constant shaking into a graduated cylinder containing 50 mils. of $\frac{N}{10}$ oxalic acid V.S. Wash the beaker with small portions of distilled water and add the washings to the contents of the cylinder. Then dilute the mixture to 100 mils and set aside to allow the precipitate to

settle. Remove 20 mils of the clear liquid (representing 0.04 gm. of the salt or 0.4 gm. of the solution) for titration. Add 5 mils of (1 : 10) sulphuric acid, warm to 80° C., and titrate with $\frac{N}{10}$ permanganate until a final drop imparts a permanent pale pink tint.

The reactions are represented by the following equations:

$$\underset{\substack{\text{Lead acetate}\\ 325.1}}{Pb(C_2H_3O_2)_2} + \underbrace{H_2C_2O_4 \cdot 2H_2O}_{126.05} = PbC_2O_4 + 2HC_2H_3O_2 + 2H_2O.$$

$$\underset{\substack{\text{Lead subacetate}\\ 548.2}}{Pb_2O(C_2H_3O_2)_2} + \underbrace{2H_2C_2O_4 \cdot 2H_2O}_{2\times 126.05} = 2PbC_2O_4 + 2HC_2H_3O_2 + 5H_2O.$$

Each mil of $\frac{N}{10}$ oxalic acid represents 0.016257 gm. of $Pb(C_2H_3O_2)_2$ or 0.013705 gm. of $Pb_2O(C_2H_3O_2)_2$, or 0.010355 gm. of Pb.

Calculate as described under assay of calcium carbonate.

The U.S.P. IX Method is essentially the same as the foregoing. It is as follows:

Assay of Lead Acetate. Dissolve an accurately weighed quantity of lead acetate (say 5 gms.) in sufficient recently boiled distilled water to make 100 mils of solution. Mix 10 mils of this solution with 50 mils of tenth-normal oxalic acid V.S. in a 200-mil measuring flask, agitate the mixture thoroughly for five minutes, then fill the flask to the 200-mil mark with distilled water; filter, and titrate 100 mils of the filtrate (representing one-twentieth of the amount of lead acetate originally taken) with tenth-normal potassium permanganate V.S., the filtrate being previously acidulated with 10 mils of sulphuric acid and warmed to 80° C.

Assay of Lead Oxid (PbO = 223.10). Dissolve about 0.4 gm. of lead oxid in 4 mils of acetic acid and 25 mils of recently boiled distilled water. Add 50 mils of tenth-normal oxalic acid V.S. and dilute with distilled water to make 200 mils of fluid. Mix well and filter. Collect 100 mils of filtrate. Acidulate it with 20 mils of diluted sulphuric acid, warm the solution to 80° C. and titrate with tenth-normal potassium permanganate V.S. as in preceding assay.

Each mil of the oxalic acid V.S. corresponds to 0.011155 gm. of PbO.

c. Methods Involving a Reduction by Means of Oxalic Acid, and Retitration of the Excess of the Latter with Potassium Permanganate.

Estimation of Manganese Dioxid (MnO_2). The estimation of manganese dioxid depends upon the fact that when it is boiled with oxalic acid in the presence of sulphuric acid definite reaction takes place, as the equation shows:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

In the estimation a measured excess of oxalic acid solution is added, together with some sulphuric acid, and the mixture heated until solution is complete.

The excess of oxalic acid is then found by retitration with standard permanganate solution. It is well to use a normal oxalic acid solution and a decinormal permanganate solution.

0.5 gm. of the dioxid is a convenient quantity to operate upon. Each mil of decinormal solution represents 0.004346 gm. of MnO_2.

Example. 0.5 gm. of MnO_2 is treated with 3 mils of sulphuric acid and 10 mils of normal oxalic acid solution, which is equivalent to 100 mils of decinormal oxalic acid solution, the mixture is heated in a water-bath to 80° C. and then treated

as described above, and upon retitrating 25 mils of decinormal permanganate are required. Thus

$$100 \text{ mils} - 25 \text{ mils} = 75 \text{ mils.}$$

of $\frac{N}{10}$ oxalic acid went into reaction with the MnO_2. Then

$$75 \times 0.004346 = 0.3259 \text{ gm.}$$

d. Methods Involving a Reduction by Means of a Standardized Solution of a Ferrous Salt, and Titration of the Remaining Unoxidized Ferrous Salt, by Permanganate.

Estimation of Nitrates (Pelouze). This method consists in adding a weighed quantity of the nitrate to an acidulated solution of a ferrous salt of known strength, and, when reaction is complete, estimating the ferrous salt remaining, by titration with permanganate, or in certain cases by means of dichromate V.S. The principle upon which the method is based is, that when nitric acid or a nitrate is brought in contact with a highly acidulated solution of a ferrous salt, the former gives off oxygen, which, passing over to the ferrous salt, oxidizes it to the ferric state, while at the same time NO is evolved. The reaction is

$$\underset{\substack{\text{Nitric acid}\\ 126.02}}{2HNO_3} + 6HCl + \underset{\substack{\text{Ferrous chlorid}\\ 760.44\\ \text{Iron}\\ 334.92}}{6FeCl_2} = 3F_2Cl_6 + 4H_2O + 2NO.$$

Thus one molecular weight of nitric acid (63.01) will oxidize three molecular weights of ferrous salt, or three atoms of iron (167.46).

Either hydrochloric or sulphuric acid may be employed. The former is preferred by most operators, and it is generally

agreed that in order to attain results of sufficient precision the estimation should be done in the presence of hydrochloric acid only. In using hydrochloric acid, however, where the titrations are to be made with permanganate, certain precautions (previously mentioned) must be observed, because of the evolution of chlorin which will otherwise take place and spoil the analysis. This may be obviated by adding to the solution to be titrated an excess of manganese sulphate.

The NO which is produced during the reaction must be removed by boiling before titration with permanganate is begun. Air must be absolutely excluded during the entire process to prevent oxidation of ferrous salt by the atmospheric oxygen, as well as to prevent oxidation of NO to HNO_3, which will oxidize more ferrous salt. The exclusion of air may be partially affected by the use on the flask of a Bunsen valve stopper (see Fig. 41), but the best method is to employ an apparatus so arranged that a constant stream of CO_2 or H gas may be passed through it (see Fig. 44).

This method, although theoretically perfect, is in practice liable to great irregularities, and will give fairly good results only if the directions, especially those as to exclusion of air,

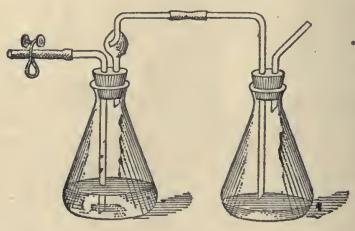

FIG. 44.

are faithfully carried out. The method of Kjeldahl is to be preferred.

To conduct the process, weigh accurately 1.5 gms. of flower

wire * free from rust (the iron content of which is known), place it an Erlenmeyer flask which is provided with a double perforated stopper fitted with two glass tubes, one of which should reach just to the surface of the liquid in the flask when in place, and the other, which is the outlet tube, should reach no lower than the bottom of the stopper. The first of these tubes is connected with an apparatus generating carbon dioxid or hydrogen, while the outlet tube serves to convey the gas into the air or into another flask containing water or an alkaline solution. 30 to 40 mils of pure fuming hydrochloric acid are added to the iron wire in the flask, gentle heat is applied, and a stream of either CO_2 or H passed through the flask and maintained throughout the entire process. When the iron is completely dissolved, the stopper is raised just long enough to introduce a small glass tube open at one end and containing the nitrate to be estimated. The quantity or nitrate taken must be equivalent to not more than 0.2 gm. of HNO_3. The stopper is then reinserted, heat applied, and gradually increased until the reaction is complete. The free hydrochloric acid liberates nitric acid from the nitrate and oxidation of a portion of the iron is effected. The ferrous chlorid is oxidized to ferric chlorid, as the equation shows, and the solution becomes at first dark brown through the presence of NO. As the heat is increased, the dark-brown color of the solution is gradually changed to yellow, as ferric chlorid is formed, and increases in intensity until the reaction is complete, then the color remains stationary and indicates completion of oxidation. The solution is now allowed to cool, but the stream of CO_2 or H gas is maintained. Forty mils of a solution of manganese sulphate are now added (this is not necessary if sulphuric acid is used instead of hydrochloric),

* Or fine piano-forte wire.

and titration with $\frac{N}{10}$ potassium permanganate solution begun, in order to determine the quantity of unaltered ferrous salt remaining in the solution. Assuming that 89 mils were required, the calculation is made as follows:

Since one molecule of HNO_3 (63.01) reacts with three atoms of iron (167.46) the quantity of iron found to have been oxidized, if multiplied by $\frac{63.01}{167.46}$, will give the quantity of nitric acid present.

Example. 1.5 gms. of iron wire, 99.6 per cent Fe = (1.494 gms. of iron), is dissolved in hydrochloric acid, as above described, and 0.6 gm. of potassium nitrate, KNO_3 (101.11), added. After oxidation, 98 mils of decinormal permanganate were required. Each mil of $\frac{N}{10}$ $KMnO_4$ = 0.005582 gm. of Fe.

0.005582 gm. × 98 = 0.547 gm. of oxidized iron. 1.494 gms. of iron were originally taken.

Therefore,

$$\frac{1.494}{0.547}{}_{0.947} \text{ gm.} = \text{the quantity of iron oxidized.}$$

Then

$$\frac{0.947 \times 63.01}{167.46} = 0.357 \text{ gm. of } HNO_3,$$

which equals

$$\frac{0.947 \times 63.01 \times 101.11}{167.46 \times 63.01} = 0.571 \text{ gm. of } KNO_3,$$

or 95.5 per cent pure.

It is usually advisable to use an $\frac{N}{5}$ instead of an $\frac{N}{10}$ $KMnO_4$ solution.

Assay of Chlorates. The chlorate is made to react with a ferrous salt, which is added to its solution in excess, and which it oxidizes to the ferric state. The unoxidized ferrous salt is then titrated with permanganate. The chlorate present being calculated from the quantity of ferrous salt which it oxidized. The method is applicable to the assay of nitrates and chromates as well.

Dissolve an accurately weighed quantity, say 0.5 gm., of potassium chlorate in sufficient distilled water to make 100 mils of solution. Take 10 mils of this solution (representing 0.05 gm.), add 25 mils of *acidulated ferrous sulphate T.S.** Place the whole in a flask provided with a Bunsen valve (see Fig. 41) and boil for ten minutes. Now cool the solution and add 10 mils of manganous sulphate T.S. and titrate the residual ferrous sulphate with tenth-normal potassium permanganate V.S. At the same time conduct a parallel experiment with another portion of 10 mils of acidulated ferrous sulphate T.S. The difference in the number of mils of the permanganate solution used in the two titrations, multiplied by 0.00204 gm., gives the weight of $KClO_3$ present.

The reaction is expressed as follows:

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 = KCl + 3Fe_2(SO_4)_3 + 3H_2O.$$
$$122.56 \quad 6\times 151.91$$

Example. In the blank experiment 25 mils of the acidulated ferrous sulphate T.S. required 26.2 mils of tenth-normal permanganate V.S.

The residual ferrous sulphate in the actual assay required 2.4 mils of the permanganate V.S., hence 23.8 mils of the per-

* Dissolve 3 gms. of clear crystals of ferrous sulphate in 90 mils of distilled water, then add sufficient sulphuric acid to make 100 mils of solution.

manganate V.S. represent the chlorate which reacted with the ferrous sulphate.

$$\frac{0.00204 \times 23.8 \times 100}{0.05} = 97.1 \text{ per cent.}$$

Chromic Acid and Chromates. Chromic acid oxidizes ferrous salts in the same manner as nitric acid does. The reaction is thus expressed:

$$\underset{5Fe=334.92}{6FeSO_4} + 6H_2SO_4 + \underset{200}{2CrO_3} = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O.$$

To an accurately weighed quantity of ferrous ammonium sulphate (Mohr's salt) $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$ (the permanganate titer of which is known), which is dissolved in a sufficient quantity of diluted sulphuric acid in an Erlenmeyer flask,* add a weighed quantity of the chromate or chromic acid in a concentrated aqueous solution. Warm the mixture on a water-bath, under a constant stream of carbon dioxid until the liquid assumes a clear green color. This occurs in a few minutes, and indicates complete reduction of the chromate.

Now allow the solution to cool, continuing the passage of carbon dioxid through the flask, and transfer the cold solution to a large beaker, and after diluting it to about 300 cc. and strongly acidifying it with sulphuric acid, titrate it for unoxidized ferrous salt by means of $\frac{N}{10}$ potassium permanganate.

It is usually sufficient to mix the solutions cold, but it is better to employ heat after mixing. A large excess of

* This flask should be provided with a stopper having two perforations through which glass tubes are passed, one of these, which serves to convey carbon dioxid gas, should reach close to the surface of the liquid, the other tube should end just below the stopper and serve as the outlet tube. See Fig. 44.

ferrous salt is unnecessary. It is imperative to dilute the solution highly before titration, as then only can the end color point be accurately determined in the green solution. The use of an excess of sulphuric acid before titration is likewise demanded. A violet-red color marks the end-point, and unless too great a quantity of chromate be taken, or the solution be insufficiently diluted, it can be easily recognized. This method is applicable not only to free chromic acid and soluble chromates, but also to chromates which are insoluble in water.* It can therefore be employed for the indirect estimation of such bases as are precipitable by chromic acid, out of neutral, ammoniacal or acetic acid solutions, as for instance lead, bismuth and barium.

Finally, the method may be employed for the estimation of chromic oxids. The solution of the latter is treated with an excess of sodium carbonate, bromine water added, and heat applied until a clear solution results. This solution, which contains all of the chromium in the form of sodium chromate, is evaporated, the residue dissolved in dilute acetic acid and the chromium completely precipitated by means of lead acetate. The precipitated lead chromate is then treated as above.

The calculation is made with reference to the equation, in which it is shown that one molecule, 100 of chromic oxid (CrO_3), is equivalent to three molecules (167.46) of metallic iron. The quantity of iron oxidized, multiplied by $\frac{100}{167.46}$, gives the weight of chromic oxid present, and from this its equivalent in potassium, sodium, lead, bismuth or barium chromate is calculated.

* In the case of insoluble chromates the salt is shaken directly with the ferrous solution, and the mixture more highly diluted, and more strongly heated, than in the case of soluble salts.

In the case of potassium dichromate ($K_2Cr_2O_7$) one molecule (294.2) is equivalent to six atoms (334.92) of metallic iron. The quantity of iron oxidized is multiplied by $\frac{294.2}{334.92}$.

Example. To 1.5 gms. of ammonio-ferrous sulphate (containing 0.2142 gm. Fe) add 0.1241 gm. of $K_2Cr_2O_7$ (molecular weight 294.2), and after complete oxidation, titrate the solution with $\frac{N}{10}$ $KMnO_4$ to determine the quantity of unchanged ferrous salt. Thirteen mils are required. Each mil represents 0.005582 gm. of Fe.

Thus, 13×0.005582 gm. $= 0.0725$ gm., the quantity of iron which was *not.* oxidized by the dichromate. This, deducted from the quantity of iron originally added ($0.2142 - 0.0725 = 0.1417$ gm.), gives the quantity which *was* oxidized.

Then,

$$\frac{0.1417 \times 100}{167.46} = 0.08475+ \text{ gm. of } CrO_3$$

or

$$\frac{0.1417 \times 294.2}{334.92} = 0.1247 \text{ gm. of } K_2Cr_2O_7.$$

Example. To 1.5 gms. of ammonio-ferrous sulphate (containing 0.2142 gm. of Fe) add the precipitate of barium chromate obtained from 0.2491 gm. of $BaCl_2 + 2H_2O$ (molecular weight 244.29) and after complete oxidation, titrate with $\frac{N}{10}$ permanganate. 7.8 mils are consumed, thus $7.8 \times 0.005582 = 0.04353$ gm. the quantity of unoxidized iron present. Then $0.2142 - 0.04353 = 0.17057$ gm. of iron oxidized by the barium chromate.

$$\frac{0.17057 \times 244.29}{167.46} = 0.2489 \text{ gm. } BaCl_2 + 2H_2O.$$

Volumetric Analysis by Means of Potassium Dichromate

In some respects the dichromate possesses advantages over permanganate:

1. It may be obtained in a pure state.

2. Its solution does not deteriorate upon standing as does that of permanganate.

3. It is not decomposed by contact with rubber as the permanganate is, and may therefore be used in Mohr's burette. Its great disadvantage, however, is that when used in the estimation of ferrous salts the end-reaction can only be found by using an external indicator. The indicator which must be used is freshly prepared potassium ferricyanid T.S., a drop of which is brought in contact with a drop of the solution being tested, on a white slab, at intervals during the titration, the end of the reaction being the cessation of the production of the blue color, when the two liquids are brought together. Thus the estimation by potassium dichromate is cumbersome, and very exact results are not as easily obtained as with permanganate.

Besides ferrous salts, a great many other substances may be estimated by oxidation analysis with dichromate. Among them nitrates, sulphates, arsenous acid, barium, lead, ferric salts after reduction by stannous chlorid or an alkaline sulphite, but not after reduction by means of metallic zinc The presence of the dissolved zinc salt interferes with the reaction of the ferricyanid indicator. Ferrous salts may be estimated in the presence of hydrochloric acid, by means of dichromate, without the precautions that apply in the case of permanganate. Chromium as chromate may be indirectly estimated; an excess of a solution of a ferrous salt being added and then the excess determined by dichromate. Iodids, thiosulphates and alkalies may also be estimated by means of potassium dichromate.

Preparation of Decinormal $\frac{N}{10}$ Potassium Dichromate

($K_2Cr_2O_7 = 294.2$; $\frac{N}{10}$ V.S. = 4.903 gms. in 1000 mils).

4.903 gms. of pure potassium dichromate * which has been pulverized and dried at 120° C. is dissolved in sufficient water to make 1000 mils of solution.

It will be noticed that $\frac{1}{60}$ of the molecular weight of the dichromate (expressed in grams) is taken in the preparation of 1000 mils of this solution. The reason for this is that one molecule of potassium dichromate when treated with an acid yields three atoms of nascent oxygen which are available for oxidizing purposes, thus

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + O_3;$$

and since each atom of oxygen is equivalent to two atoms of hydrogen, one molecule of the dichromate must be equivalent to six atoms of hydrogen. Hence a normal solution of potassium dichromate, when used as an oxidizing agent, should contain one-sixth of the molecular weight, expressed in grams, in 1000 mils (see definition for normal solution) and its deci normal solution $\frac{1}{60}$.

If a standard solution of potassium dichromate is to be made for use as precipitant, as in the titration of barium, one-fourth of the molecular weight is to be taken for 1000 mils of the normal solution, as explained in Chapter III.

Standard solution of potassium dichromate is sometimes used as a neutralizing solution for estimating alkalies, phenolphthalein being used as indicator.

When used for this purpose the normal solution contains 147.1 gms. in 1 liter (one-half the molecular weight

* Potassium dichromate for use in volumetric analysis should respond to all the tests for purity given in the U.S.P., or it should be recrystallized several times and then dried.

in grams). It is then the exact equivalent of any normal acid V.S.

$$\underset{2)112.2}{2KOH} + \underset{2)294.2}{K_2Cr_2O_7} = 2K_2CrO_4 + H_2O.$$

56.1 gms. 147.1 gms., or 1000 mils normal V.S.

Decinormal potassium dichromate may also be used in conjunction with potassium iodid and sulphuric acid for standardizing sodium thiosulphate. Iodin is liberated from potassium iodid in this reaction. The reaction is expressed by the equation

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2.$$

Thus one molecule of the dichromate will liberate six atoms of iodin, therefore a normal solution should contain one-sixth of the molecular weight, and a decinormal solution $\frac{1}{60}$ in 1000 mils. The solution is hence of the same strength as that which is used for oxidizing purposes. If the decinormal solution containing 14.71 gms. in 1 liter is used, it has the effect of a $\frac{3N}{10}$ solution.

The decinormal solution which is used as an oxidizing agent is chemically equivalent to decinormal potassium permanganate. When used for the purpose of liberating iodin from potassium iodid, it is the equivalent of an equal volume of decinormal sodium thiosulphate.

Standard potassium dichromate may be checked in the same way as standard permanganate, with pure iron wire.

ESTIMATION OF FERROUS SALTS WITH POTASSIUM DICHROMATE

For titrating ferrous salts the decinormal solution of dichromate is used in the following manner:

Make an aqueous solution of the ferrous salt, introduce

it into a flask, and acidulate it with sulphuric or hydrochloric acid. Now add gradually from a burette the decinormal potassium dichromate until a drop taken out upon a white slab no longer shows a blue color with a drop of freshly prepared potassium ferricyanid T.S. Note the number of mils of the standard solution used, multiply this number by the factor, and thus obtain the quantity of pure salt in the sample taken.

Ferrous salts strike a blue color with potassium ferricyanid, but as the quantity of ferrous salt gradually diminishes during the titration, the blue becomes somewhat turbid, acquiring first a green, then a gray, and lastly, a brown shade. The process is finished when the greenish-blue tint has entirely disappeared.

The reaction of potassium dichromate with ferrous salts always takes place in the presence of free sulphuric or hydrochloric acid at ordinary temperatures. Nitric acid should not be used.

If it is desired to estimate ferric salts by this standard solution it is necessary to first reduce them. This may be done by metallic magnesium, sulphurous acid, the alkali sulphites, or by stannous chlorid.

One molecule of potassium dichromate yields, under favorable circumstances, 3 atoms of oxygen. This is shown by the following equation:

$$K_2Cr_2O_7 = Cr_2O_3 + K_2O + O_3.$$

Here it is seen that the three liberated atoms of oxygen combine at once with the ferrous oxid, converting it into ferric oxid:

$$6FeO + O_3 = Fe_6O_9 \quad \text{or} \quad 3Fe_2O_3.$$

In the oxidation of a ferrous salt, the reaction takes place only in the presence of an acid.

The dichromate then gives up its oxygen. Four of its oxygen atoms combine at once with the replaceable hydrogen of the accompanying acid, the other three being liberated. The three oxygen atoms thus set free are available either for direct oxidation or for combination with the hydrogen of more acid. In the latter case a corresponding quantity of acidulous radicals is set free.

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + O_3.$$

In this case four of the liberated atoms of oxygen combine with eight of the atoms of hydrogen of sulphuric acid and liberate four SO_4 radicals, which at once combine with the K_2 and Cr_2 of the dichromate. The other three atoms are set free. If seven sulphuric acid molecules are used instead of four molecules, the three free atoms of oxygen will liberate $3(SO_4)$:

$$K_2Cr_2O_7 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + (SO_4)_3.$$

If this liberation of $3(SO_4)$ takes place in the presence of a ferrous salt, the $3(SO_4)$ will combine with six molecules of the ferrous salt, converting it into a ferric salt:

$$6FeSO_4 + 3SO_4 = Fe_6(SO_4)_9 = 3Fe_2(SO_4)_3;$$

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + [3Fe_2(SO_4)_3].$$

If in the above case hydrochloric acid is used instead of sulphuric, fourteen molecules of the former must be taken to supply the neccessary hydrogen.

The seven liberated atoms of oxygen must have fourteen atoms of hydrogen to combine with.

Three of these atoms of oxygen liberate six univalent or three bivalent acidulous radicals.

Therefore, since one molecule of $K_2Cr_2O_7$ will give up for oxidizing purposes three atoms of oxygen, which are equivalent chemically to six atoms of hydrogen, one-sixth of the molecular weight in grams of the dichromate, dissolved in sufficient water to make one liter, constitutes a normal solution, and one-tenth of this quantity of $K_2Cr_2O_7$ in a liter, a decinormal solution.

Thus the estimation of ferrous salts is effected by oxidizing them to ferric with an oxidizing agent of known power, the strength of the ferrous salt being determined by the quantity of the oxidizing agent required to convert it to ferric.

Saccharated Ferrous Carbonate ($FeCO_3 = 115.82$). One gm. of saccharated ferrous carbonate is dissolved in 10 mils of diluted sulphuric acid and the solution diluted with water to about 100 mils. The decinormal potassium dichromate is carefully added, until a drop of the solution taken out and brought in contact with a drop of freshly prepared solution of potassium ferricyanid ceases to give a blue color.

The number of mils of the dichromate solution is read off and the following equations applied:

$$\underset{694.9}{6FeCO_3} + 6H_2SO_4 = \underset{911.34}{6FeSO_4} + 6H_2O + 6CO_2;$$

then

$6FeCO_3$ or $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4$

$6)694.9$ $6)911.34$ $6)294.2$

$10)115.84$ $10)151.89$ $10)49.03$

11.584 gms. 15.189 gms. 4.903 gms., or 1000 mils $\frac{N}{10}$ $K_2Cr_2O_7$ V.S.

$$= K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3.$$

Thus each mil of $\frac{N}{10}$ $K_2Cr_2O_7$ represents 0.011584 gm. of pure ferrous carbonate or 0.005582 gm. of metallic iron.

If strong sulphuric acid is added to saccharated ferrous carbonate it will char the sugar, and a black mass of burnt sugar is obtained. This may be prevented by adding water first, and then, slowly, the sulphuric acid.

Instead of sulphuric acid, hydrochloric acid may be used.

FIG. 45.

This will not char the sugar, but the ferrous chlorid which is then formed is too readily oxidized by the air.

It has also been suggested that as hydrochloric acid so rapidly converts ordinary sugar into invert sugar as to render it easily attacked by the dichromate, it should be cautiously used, if at all. Phosphoric acid has none of these disadvantages, and may be employed with good results.

In making estimations of ferrous salts with potassium dichromate, care should be taken to avoid atmospheric oxidation. It is good practice to calculate approximately how much of the standard solution will probably be required to

complete the oxidation, and then add almost enough of the standard solution at once, instead of adding it slowly.

A white porcelain slab is then got ready, and placed alongside of the flask in which the titration is to be performed. Upon this slab are placed a number of drops of the freshly prepared solution of potassium ferricyanid, and at intervals during the titration a drop is taken from the flask on a glass rod and brought in contact with one of the drops on the slab. The glass rod should always be dipped in clean water after having been brought in contact with a drop of the indicator. See Fig. 45.

When a drop of the solution ceases to give a blue color on contact with the indicator, the reaction is complete.

Pills of ferrous carbonate and mass of ferrous carbonate are assayed by the same process.

Ferrous Sulphate ($FeSO_4+7H_2O=277.89$). Dissolve about one gram of crystallized ferrous sulphate in a little water, add a good excess of sulphuric or hydrochloric acid, titrate with the decinormal potassium dichromate, as directed under Ferrous Carbonate, and apply the following equation:

$$6(FeSO_4.7H_2O) + K_2Cr_2O_7 + 7H_2SO_4$$

$$6)1667.34$$
$$10)277.89$$
$$27.789 \text{ gms., or } 1000 \text{ mils } \frac{N}{10} K_2Cr_2O_7 \text{ V.S.}$$

$$= 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 49H_2O.$$

Thus each mil of the $\frac{N}{10} K_2Cr_2O_7$ V.S. represents 0.027789 gm. of crystallized ferrous sulphate or 0.015189 anhydrous. If 1 gm. of the salt is taken and dissolved as above, it should require about 37 mils of the standard solution, equivalent to about 100 per cent.

TABLE OF SUBSTANCES WHICH MAY BE ESTIMATED BY MEANS OF POTASSIUM PERMANGANATE OR POTASSIUM DICHROMATE.

Name.	Formula.	Molecular Weight.	$\frac{N}{10}$ Factor.
Acid, chromic	CrO_3	100	0.0033
" hypophosphorous	HPH_2O_2	66.04	0.001651
" nitric	HNO_3	63.01	0.0021
" nitrous	HNO_2	47.01	0.00235
" oxalic (crystallized)	$H_2C_2O_4+2H_2O$	126.05	0.0063
Barium dioxid	BaO_2	169.37	0.00845
Calcium chlorid	$CaCl_2$	111.01	0.00555
" hypophosphite	$Ca(PH_2O_2)_2$	170.17	0.002127
Ferric chlorid	$FeCl_3$	162.20	0.01622
" hypophosphite	$Fe(PH_2O_2)_3$	250.94	0.025094
" sulphate	$Fe_2(SO_4)_3$	399.85	0.01999
Ferrous carbonate	$FeCO_3$	115.82	0.011582
" oxid	FeO	71.82	0.007182
" sulphate (anhydrous)	$FeSO_4$	151.89	0.015189
" " (crystallized)	$FeSO_4+7H_2O$	277.89	0.027789
Ferrum (metallic)	Fe_2	55.82	0.005582
Hydrogen dioxid	H_2O_2	34.0	0.0017
Manganese dioxid	MnO_2	86.93	0.004346
Potassium hypophosphite	KPH_2O_2	104.15	0.0026
Sodium hypophosphite	$NaPH_2O_2$	88.05	0.0022
" nitrite	$NaNO_2$	69.01	0.00345

Analysis by Indirect Oxidation

This method of analysis is based upon the oxidizing power of iodin.

Iodin acts upon the elements of water, forming hydriodic acid with the hydrogen, and liberating oxygen in a nascent state.

Nascent oxygen is a [illegible] active agent, and readily combines with and oxidizes [illegible] substances, such as arsenous oxid, sulphurous acid, sulphites, thiosulphates, hydrosulphuric acid, the lower oxids of antimony and their salts.

$$As_2O_3 + 2H_2O + 2I_2 = As_2O_5 + 4HI;$$
$$H_2SO_3 + H_2O + I_2 = 2HI + H_2SO_4.$$

Therefore iodin is said to be an indirect oxidizer, and may be used for the estimation of a great variety of substances with extreme accuracy.

When iodin is brought in contact with certain oxidizable substances it is decolorized. This decolorization occurs as long as some of the oxidizable substance is present, and ceases when oxidation is complete. Hence when the yellow color of iodin shows itself in the solution being analyzed the reaction is known to be at an end. In most cases a more delicate end-reaction is obtained by using starch solution as an indicator. This gives a distinct and unmistakable blue color with the slightest excess of iodin.

In making an analysis with standard iodin solution, the substance under examination is brought into dilute solution (usually alkaline), the starch solution added, and then the iodin, in the form of a standard solution, is delivered in from a burette, stirring or shaking constantly, until a final drop colors the solution blue—a sign that a slight excess of iodin has been added.

Preparation of Decinormal Iodin ($I = 126.92$; $\frac{N}{10}$ V.S. = 12.692 gms. per liter). Dissolve 12.692 gms. of pure * iodin

* If pure iodin be not at hand, it may be prepared from the commercial article as follows:

Powder the iodin and heat in it a porcelain dish placed over a water-bath, stirring constantly with a glass rod for twenty minutes. Any adhering moisture, together with any cyanogen iodid, and most of the iodin bromid and iodin chlorid, is thus vaporized.

Then triturate the iodin with about 5 per cent of its weight of pure, dry potassium iodid. The iodin bromid and chlorid are thereby decomposed, potassium bromid and chlorid being formed and iodin liberated from the potassium iodid.

The mixture is then returned to the porcelain dish, covered with a clean glass funnel, and heated on a sand-bath. A pure resublimed iodin is then obtained.

in 300 mils of distilled water containing 18 gms. of pure potassium iodid. Then add enough water to make the solution measure at 25° C. exactly 1000 mils.

The solution should be kept in small glass-stoppered vials, in a dark place.

The potassium iodid used in this solution acts merely as a solvent for the iodin.

If pure iodin is used in making this solution, there is no necessity for checking (standardizing) it.

But if desired the solution may be checked against pure arsenous acid or sodium thiosulphate. It there is any doubt as to the purity of the iodin, it is best to take a larger quantity, say 14 gms. instead of the 12.692 gms. directed above, and then dilute the resulting solution to the proper strength after standardizing.

Standardization of Iodin V.S. by Means of a Decinormal Sodium Thiosulphate Solution. 25 mils of the iodin solution are accurately measured off into a beaker, and then from a burette the $\frac{N}{10}$ thiosulphate is delivered until the solution is of a pale yellow color, two or three drops of starch solution are then added, and the titration with the thiosulphate solution continued until the blue color of starch iodid is discharged.

If the iodin solution is exactly decinormal, the 25 mils will require 25 mils of decinormal sodium thiosulphate to exactly complete the reaction.

If on the other hand more than 25 mils of thiosulphate solution is required, it indicates that the iodin solution is too concentrated, and must be diluted so as to correspond with the thiosulphate solution, volume for volume.

Example. Assuming that in the above titration, 27 mils of the thiosulphate solution were used, then each 25 mils of the

iodin solution must be diluted with water to make 27 mils in order to convert the iodin solution into a strictly decinormal solution. If, however, the iodin solution is found to be weaker, as evidenced by its using up less than its own volume of $\frac{N}{10}$ thiosulphate, its relative strength should be noted on the label of the container.

Thus if only 24.8 mils of the thiosulphate solution are used up, then 1 mil of the latter equals $\frac{25}{24.8}$ mils or 1.008 mils of the iodin solution.

One mil of this iodin solution is equivalent to 0.992 mil of $\frac{N}{10}$ thiosulphate, which is the same as saying 1 mil = 0.992 mil of $\frac{N}{10}$ iodin, or expressed in another way, 1 mil of this iodin solution contains 0.01259+ gm. of iodin.

Such an iodin solution may be used as an empirical solution, and in any assay the quantity of it (in mils) which is consumed is divided by 1.008 or multiplied by $\frac{24.8}{25}$ or by 0.992, and then multiplied by the decinormal factor for the substance analyzed. Another way is to multiply the mils of this iodin solution used by the weight of iodin contained in each mil, and then by a fraction in which the numerator represents the quantity of the substance analyzed equal to an atom of iodin, and the denominator is the atomic weight of iodin.

Example. 0.1 gm. of arsenous acid consumes 20 mils of this empirical solution. How much absolute As_2O_3 does it contain? The $\frac{N}{10}$ factor for As_2O_3 is 0.004948 gm.

$$\textit{Method (a)} \quad \frac{20 \times 0.004948}{1.008} = 0.0981 \text{ gm.}$$

Method (*b*) $20 \times \frac{24.8}{25} \times 0.004948 = 0.0981$ gm.

Method (*c*) $20 \times 0.992 \times 0.004948 = 0.0981$ gm.

Method (*d*) $20 \times 0.01259 \times \frac{49.48}{126.92} = 0.0981$ gm.

It is a good plan to have the factors marked on the labels. In the above case the label may be marked

$\times \frac{24.8}{25}$ or $\times 0.992$ or 1 mil $= 0.01259$ gm. iodin.

Standardization of Iodin V.S. by Means of Arsenous Oxid. 0.2 gm. of pure resublimed vitreous arsenous oxid is weighed off very carefully into a flask 50 mils of water are added, and then, after the addition of 2 gms. or more of sodium bicarbonate, the mixture is gently warmed and shaken until the arsenous oxid is completely dissolved.*

To this solution a few drops of starch indicator are added, and then the iodin solution delivered carefully from a burette until a blue color marks the end of the reaction.

$$\underset{197.92}{As_2O_3} + \underset{4 \times 126.92}{I_4} + 2H_2O = As_2O_5 + 4HI.$$

49.48 gms. of $As_2O_3 = 126.92$ gms. of iodin;

4.948 " " $As_2O_3 =$ 12.692 " " " or 1000 mils $\frac{N}{10}$ V.S.

* Arsenous oxid is much more readily soluble in alkali hydroxid, than in carbonated alkalies, therefore the following method of making the solution is preferred: 0.2 gm. of arsenous oxid is dissolved in a small quantity of boiling water with the aid of potassium hydroxid (free from sulphur), the solution is then acidified with hydrochloric acid, and then again made alkaline by the addition of sodium bicarbonate. The latter must be added in considerable excess, being careful, however, to avoid loss of solution during effervescence.

0.2 gm. of As_2O_3 will require

$$\frac{1000 \times 0.2}{4.948} = 40.44 \text{ mils of a true } \frac{N}{10} \text{ iodin V.S.}$$

Assuming that in the above titration 37.4 mils of the iodin solution were used, then the iodin solution is too concentrated and must be diluted so that each 37.4 mils will be made up to 40.44 mils.

After diluting in this way a new trial should be made.

It is a good plan to make a decinormal solution of the arsenous oxid by dissolving 4.948 gms. of the pure oxid and 30 gms. of sodium bicarbonate in sufficient water to make 1000 mils at 15° C. and to titrate this with the iodin solution. 25 mils of this solution should require for complete oxidation exactly 25 mils of the iodin solution, if the latter is strictly of decinormal strength.

The Starch Solution. This solution, which is used as an indicator in iodometric determinations, is made as follows:

One gm. of starch (potato, arrowroot, or corn starch) is triturated with 10 mils of cold water, until a smooth mixture is obtained, then sufficient boiling water is added, with constant stirring, to make 200 mils of a thin, translucent fluid. If the solution is not translucent it should be boiled for about three minutes, then allowed to cool, and filtered. This solution does not keep very long, in fact it becomes useless after standing one day, therefore it should be freshly prepared when required.

This indicator is very sensitive to iodin—it will detect one part of iodin in 3,500,000. If the solution is not clear, or contains flocks of insoluble starch, the characteristic beautiful blue color is not obtained with iodin; instead, a greenish or brownish color is produced, and the insoluble

particles are even colored black and are decolorized with difficulty.

The blue color which starch gives with iodin constitutes a very delicate indication of the slightest excess of iodin. This color is usually regarded as being due to the formation of a compound of starch and iodin, called iodid of starch. It is a compound of very unstable character and of doubtful composition.

Sodium thiosulphate behaves towards iodid of starch exactly as it does toward free iodin—it takes up the iodin and thus discharges the blue color.

Iodid of starch dissociates upon heating, but reunites upon cooling, hence it is advisable to avoid heat in estimations where starch is used as an indicator.

In order to prevent the deterioration of this solution a few drops of chloroform may be added; this will preserve it for a long time. Oil of cassia is also recommended as a preservative. Moerk adds 2 mils of the oil to a liter of the cooled starch solution. Zinc chlorid or iodid added to the boiling starch solution will prevent its decomposition for a long time. A starch solution so made, however, should not be used in titrations of sulphids, because zinc reacts with sulphids.

In the case of solutions containing carbonates, the precipitate of zinc carbonate is so small in amount that it does not interfere in the least with the recognition of the end-reaction tint. Mercuric iodid is also a very valuable preservative.

0.01 gm. of mercuric iodid in a liter of the starch solution is quite sufficient. A very satisfactory indicator is the commercial soluble starch which is made by heating potato starch with glycerin and precipitating the starch by repeated treatment with alcohol. This starch dissolves readily in hot water

forming a clear solution, which gives a very delicate reaction with iodin. It is best preserved under alcohol, the latter being removed by filtration and evaporation, when the starch is wanted for making a solution.

In making starch solution for use as an indicator, long continued boiling should be avoided, as this converts some of the starch into dextrin.

On the Use of Sodium Bicarbonate in Titrations with Iodin. In these titrations an excess of alkali is necessary in order to neutralize the hydriodic acid formed.

$$As_2O_3 + 2H_2O + 2I_2 = As_2O_5 + 4HI.$$

If the hydriodic acid is not removed by neutralization it will react with the arsenic oxid (As_2O_5), reducing it to arsenous oxid (As_2O_3) and liberate iodine, as shown by the following equation:

$$4HI + As_2O_5 = As_2O_3 + 2H_2O + 2I_2.$$

Sodium bicarbonate is usually employed to neutralize the HI and should be used in slight excess.

Alkali hydroxids or carbonates cannot be used for this purpose, because they react with free iodin or even with starch iodid. Bicarbonates ordinarily have no such action, and therefore sodium bicarbonate is usually directed to be added in excess to the solution to be titrated with iodin.

It is well known that sodium hydroxid solution reacts with free iodin, with formation of hypoiodite and iodid.

$$2NaOH + I_2 = NaIO + NaI + H_2O,$$

the hypoiodite quickly forming iodate.

$$3NaIO = 2NaI + NaIO_3.$$

It is also now a recognized fact that sodium carbonate

is partly hydrolyzed when in solution, with formation of some sodium hydroxid, as per equation,

$$Na_2CO_3 + H_2O = NaOH + NaHCO_3.$$

It therefore reacts in much the same way with iodin as the hydroxid, though to a less extent.

On the other hand, it is generally supposed that bicarbonate of soda is without effect on iodin, and when, in iodometric estimations, addition of sodium bicarbonate is indicated, little attention is given to amount added, as long as it be in excess.

The experiments of W. A. Puckner, Proc. A. Ph. A., 1904, 408, prove that we are entirely wrong in the supposition that sodium bicarbonate has no effect upon iodin. He showed that when using 1 to 2 gms. of the bicarbonate, an error of 1.5 to 4.5 mils of decinormal iodin may be introduced, even when the sodium bicarbonate used is of exceptional purity, and especially proven to be free from carbonate, sulphite or thiosulphate. He shows that when sodium bicarbonate is added to a decinormal iodin solution, residual titration with sodium thiosulphate will show a considerable loss of free iodin, which went into combination in some form or other (probably iodid) and that the quantity so lost is proportional to (1) the mass of sodium bicarbonate; (2) the time of the interaction (the reaction is slow); (3) the concentration of the solution; (4) the temperature, and (5) the size of the flask in which reaction occurs. These phenomena are due to the fact that sodium bicarbonate when dissolved in water undergoes hydrolysis, thus

$$2NaHCO_3 = Na_2CO_3 + H_2CO_3 \quad \text{or} \quad (H_2O + CO_2).$$

This breaking up of the $NaHCO_3$ into Na_2CO_3 and H_2CO_3, and the latter into H_2O and CO_2, continues until the

pressure of the CO_2 above is equal to the pressure of the gas in the solution, i.e., until equilibrium has been reached. In concentrated solutions of $NaHCO_3$ the amount hydrolyzed is much greater than in dilute solutions. An elevation of temperature materially increases the absorption of iodin.

Less iodin is lost when smaller flasks are used, provided the glass stopper completely shuts off communication with the atmosphere. The CO_2 will escape from the solution until its pressure in the solution is equal to that of the gas above. Thus, since a larger volume of air is contained in a larger flask, more CO_2 passes from the liquid before equilibrium is established, hence more $NaHCO_3$ is decomposed, and more iodin in consequence absorbed.*

Reasoning from the above observations it may be said that: 1, though sufficient sodium bicarbonate be used to more than neutralize the hydriodic acid formed, the solution titrated should be well diluted; 2, that the titration should be done cold; 3, that the titration should be done in small stoppered flasks, and 4, it should be done quickly.

Estimation of Arsenous Compounds

These compounds are estimated by means of iodin in a manner similar to that described under standardization of iodin solution by means of arsenous oxid. The method is as follows:

Arsenous Oxid (*Arsenous Acid, Arsenous Anhydrid, Arsenic Trioxid*) ($As_2O_3 = 197.92$). When arsenous acid is brought in contact with iodin in the presence of water and an alkali,

* For further study of equilibrium, see the work of Dr. H. N. McCoy, Am. Ch. J., vol. XXIV, 437

it is oxidized into arsenic acid and the iodin is decolorized. The reaction is:

$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI;$$

$$NaHCO_3 + HI = NaI + H_2O + CO_2.$$

The alkali should be in sufficient quantity to combine with the hydriodic acid formed, and must be in the form of potassium or sodium bicarbonate.

The hydroxids or carbonates should not be used. Starch solution is used as the indicator, a blue color being formed as soon as the arsenous acid is entirely oxidized into arsenic acid.

Dissolve about 0.2 gm. of arsenous acid accurately weighed, in 20 mils of boiling distilled water by the gradual addition of sodium hydroxid T.S. until complete solution results. Neutralize this solution with a diluted sulphuric acid V.S., using phenolphthalein T.S. as indicator, cool, dissolve in it 2 gms. of sodium bicarbonate and titrate the mixture with decinormal iodin V.S., using starch T.S. as indicator, shaking or stirring the mixture constantly until a permanent blue color is produced. The following equation illustrates the reaction:

$$\underset{\substack{4)197.92\\10)49.48\\4.948\text{ gms.}}}{As_2O_3} + \underset{}{2H_2O} + \underset{\substack{4)507.68\\10)126.92\\12.692\text{ gms. or 1000 mils }\frac{N}{10}\text{ I V.S.}}}{2I_2} = 4HI + As_2O_5.$$

Thus each mil of $\frac{N}{10}$ I V.S. represents 0.004948 gm. of pure As_2O_3.

Solution of Arsenous Acid and Solution of Potassium Arsenite are assayed in the manner above described. Twenty mils are taken for the assay, 1 gm. of sodium bicarbonate

added, the solution diluted to 100 mils, and titrated with the decinormal iodin solution. No indicator is required though starch may be used.

In the case of solution of potassium arsenite, it is advisable to slightly acidify with hydrochloric acid, then to make the solution alkaline with sodium bicarbonate before titrating. The hydrochloric acid is employed here in order to neutralize any potassium hydroxid which may have been formed through hydrolysis of the potassium bicarbonate contained in the solution.

Arsenous Iodid ($AsI_3 = 455.72$). This salt is estimated in the same way as described for arsenous oxid. The reaction is illustrated by the following equation:

$$2AsI_3 + 5H_2O + 2I_2 =. As_2O_5 + 10HI.$$

$$4)911.44$$
$$10)227.86$$
$$22.786 \text{ gms.} = 1000 \text{ mils } \frac{N}{10} \text{ I V.S.}$$

The Direct Percentage Assay of Arsenous Compounds. A quantity of arsenous acid is taken, which is equal to the weight of pure As_2O_3, oxidized by 100 mils of decinormal iodin, i.e., 0.4948 gm.

If 0.4948 gm. of the sample be taken then each mil of $\frac{N}{10}$ I V.S. will represent $\frac{1}{100}$ of this quantity or 1 per cent of pure As_2O_3. In the case of weak solutions of arsenic, as liquor acidi arsenosi, liquor potassii arsenitis, etc., which contain only one per cent of arsenous acid. A much larger quantity should be taken for analysis, otherwise the quantity of standard iodin solution used will be so small as to diminish the accuracy of the test.

Thus, if only 0.4948 gm. of either of the above solutions

be taken, no more than 1 mil of the standard solution would be required. It is better to take enough of the preparation to use up 30 to 50 mils of standard solution.

Estimation of Antimony Compounds

Antimonous oxid (Sb_2O_3) or any of its compounds may be accurately estimated by means of iodin, in a manner similar to that described for the estimation of arsenous oxid, the antimonous oxid being oxidized to antimonic oxid, as per equation,

$$Sb_2O_3 + 2H_2O + 2I_2 = 4HI + Sb_2O_5.$$

The antimonous oxid is dissolved and kept in solution by the aid of tartaric acid, and then after the addition of an excess of sodium-bicarbonate, the solution is titrated with $\frac{N}{10}$ iodin, using starch as an indicator. Accurate results can only be obtained if the solution is sufficiently alkaline to neutralize the hydriodic acid formed during the reaction. The titration should be conducted without delay after the addition of the bicarbonate, otherwise a precipitate of antimonous hydrate will be formed, upon which iodin has little effect. The antimony must be in solution to be properly attacked by the iodin.

To 0.1 gm. of antimonous oxid 20 mils of water are added and the mixture heated to boiling; to this tartaric acid is added in small portions at a time until the oxid is completely dissolved. The solution is then neutralized by means of sodium carbonate, and sufficient of a saturated solution of sodium bicarbonate is added to make the solution distinctly alkaline (about 10 mils is required for 0.1 gm. of the antimonous oxid). The mixture is now ready for titration with standard

iodin solution. This should be done immediately. The appearance of a permanent blue color marks the end-point, starch being used as indicator.

$$Sb_2O_3 + 2H_2O + 2I_2 = 4HI + Sb_2O_5.$$

$4)288.4$ $\qquad$ $4)507.68$

$10)72.1$ $\qquad$ $10)126.92$

7.21 gms. $\qquad$ 12.692 gms. or 1000 mils $\frac{N}{10}$ V.S.

One mil of $\frac{N}{10}$ iodin represents 0.00721 gm. of Sb_2O_3.

The solution of the oxid may be made by means of hydrochloric acid, and after adding a portion of tartaric and diluting with water, sodium bicarbonate is added and the titration conducted as above.

Other compounds of antimony may be estimated in the same way. Antimonic compounds are reduced to antimonous sulphid (Sb_2S_3) by precipitating with hydrogen sulphid, and after thoroughly washing the precipitate, dissolving it in hydrochloric acid; thus a solution of antimonous chlorid is obtained from which all traces of hydrogen sulphid are expelled by boiling. This solution is diluted with water, tartaric acid added, and finally, after making alkaline with sodium bicarbonate, titrated with the standard iodin solution as above described.

Antimony and Potassium Tartrate (Tartar Emetic) $[2(K[SbO]C_4H_4O_6)+H_2O=664.7]$. One gm. of the salt is dissolved in sufficient water to make 100 mils. 30 mils of this solution, representing 0.3 gm. of the salt, are taken for assay. 20 mils of a cold saturated solution of sodium bicarbonate are added, then a little starch solution, and the mixture titrated with $\frac{N}{10}$ iodin until a permanent blue color appears.

The calculation is as follows:

$$\underbrace{2K(SbO)C_4H_4O_6 + H_2O}_{\substack{4)664.7\\10)166.17\\16.617\text{ gms.}}} + \underbrace{2I_2}_{\substack{4)507.68\\10)126.92\\12.692\text{ gms.}=1000\text{ mils }\frac{N}{10}\text{ I V.S.}}} + 3H_2O$$

$$= 4HI + 2KHC_4H_4O_6 + 2HSbO_3.$$

1 mil of $\frac{N}{10}$ iodin represents 0.016617 gm. of $K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$ (crystallized tartar emetic).

$K(SbO)C_4H_4O_6$ (anhydrous tartar emetic) = 323.34.

$$\begin{array}{l} 2)323.34 \\ 10)161.67 \\ 16.167\text{ gms.} = 1000\text{ mils }\frac{N}{10}\text{ V.S.} \end{array}$$

Thus 1 mil of $\frac{N}{10}$ iodin represents 0.016167 gm. of anhydrous tartar emetic.

Estimation of Sulphurous Acid and Sulphites

These substances may be accurately estimated by means of a standard solution of iodin. When sulphurous acid or one of its salts is brought in contact with iodin, a complete oxidation takes place. The sulphurous acid is oxidized to sulphuric acid and the sulphite to a sulphate, as the equations show:

$$H_2SO_3 + H_2O + I_2 = 2HI + H_2SO_4,$$

$$Na_2SO_3 + H_2O + I_2 = 2HI + Na_2SO_4,$$

$$NaHSO_3 + H_2O + I_2 = 2HI + NaHSO_4.$$

There are two methods which may be employed. In one method the substance is brought into solution in water, an excess of sodium bicarbonate is added, and then the standard iodin solution is run in until a faint yellow color of free iodin

marks the end-reaction. If starch solution is used as indicator the end-point is the production of a blue color. The other method is that of Giles and Shearer, who, in a very voluable series of experiments detailed in the J. S. C. I., III, 197, and IV, 303, suggest the following modification:

The weighed sulphurous acid or the sulphite (in fine powder) is added to an accurately measured excess of $\frac{N}{10}$ iodin, without diluting with water. After the mixture has been allowed to stand for about one hour, with frequent shaking, the oxidation is complete, and the excess of iodin is ascertained by titrating back with $\frac{N}{10}$ sodium thiosulphate.

The quantity of the latter deducted from the quantity of $\frac{N}{10}$ iodin solution added, will give the quantity of the latter which reacted with the sulphite.

The neutral and acid sulphites of the alkalies, alkali earths, and even zinc and aluminum, may be accurately estimated in this manner. The less soluble salts requiring, of course, more time and shaking, to insure their complete oxidation. The latter is the U. S. P. method.

Sulphurous Acid. This is an aqueous solution of sulphur dioxid ($SO_2 = 64.07$).

Sulphurous acid when brought in contact with iodin is oxidized into sulphuric, the iodin being decolorized because of its union with the hydrogen of the accompanying water, forming hydriodic acid.

Two grams of sulphurous acid are taken and diluted with distilled water (recently boiled and cooled *) to about 25

* "Recently boiled" insures absence of air, the oxygen of which would partially oxidize the sulphurous acid, and "cooled" is directed to avoid loss of SO_2, which would occur if hot water were used.

mils. Two grams of sodium bicarbonate are added, and then the decinormal iodin V.S. is delivered into the solution (to which a little starch solution had been previously added) until a permanent blue color is produced.

The following equations, etc., show the reactions that take place:

$$H_2SO_3 + H_2O + I_2 = 2HI + H_2SO_4.$$

Sulphurous acid being, however, looked upon as a solution of SO_2 in water, the quantity of this gas is generally estimated in analyses.

$$\underbrace{H_2O,SO_2}_{\substack{2)64.07 \\ 10)32.04 \\ 3.204 \text{ gms.}}} + H_2O + \underbrace{I_2}_{\substack{2)253.84 \\ 10)126.92 \\ 12.692 \text{ gms.}}} = 2HI + H_2SO_4.$$

Thus each mil of $\frac{N}{10}$ iodin consumed before the blue color appears, represents 0.003204 gm. of SO_2.

The Residual Method. Because of the volatile nature of this acid the residual method described below is the most satisfactory in that loss by volatilization is avoided and complete oxidation of the acid assured. When the direct method described is used there is more or less loss of SO_2 and incomplete oxidation, with separation of sulphur.

Measure 2 mils of the sulphurous acid into a stoppered weighing flask and find its exact weight. Add this to the 50 mils of $\frac{N}{10}$ iodin contained in a titration flask and let the solution stand for about five minutes. Then titrate with $\frac{N}{10}$ sodium thiosulphate until the mixture is decolorized. Subtract the number of mils of the thiosulphate used from the

50 mils of $\frac{N}{10}$ iodin added, and multiply the difference by the $\frac{N}{10}$ factor for SO_2, which is 0.0032035 gm. This will give the weight of SO_2 in the quantity of acid taken for analysis.

When a solution containing sulphur dioxid is to be measured by means of a pipette, it is never advisable to fill the instrument by suction in the usual manner, as this would cause a loss of the gas. A better plan is to fill the pipette by pressure by the use of an arrangement similar to that shown in Fig. 46.

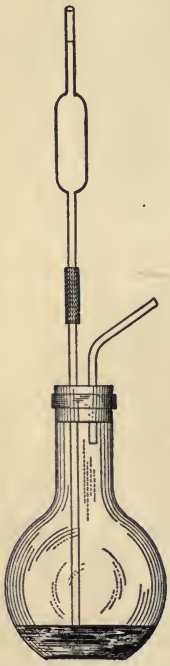

FIG. 46.

The solution containing sulphur dioxid or other volatile substance is poured into a flask which is provided with a stopper through which two glass tubes pass; one of these tubes reaches nearly to the bottom of the flask and the other projects about one-half an inch below the stopper and is bent outward above. To the upper end of the former the pipette is attached by means of a piece of rubber tubing. By blowing into the flask through the shorter tube the liquid is caused to rise and fill the pipette, which may then be easily pulled out of the rubber tube connection.

Sodium Sulphite ($Na_2SO_3+7H_2O=252.2$). Take 0.5 gm. of the finely powdered crystals, add to 50 mils of $\frac{N}{10}$ iodin, contained in a 100-mil glass-stoppered flask, and allow to stand for one hour (shaking frequently); then titrate with $\frac{N}{10}$ sodium thiosulphate until the color is discharged.

The reaction is expressed as follows:

$$\underbrace{Na_2SO_3 + 7H_2O}_{} + I_2 = 2HI + Na_2SO_4 + 6H_2O.$$

$$\begin{array}{l} 2)252.2 \\ 10)126.1 \\ \hline 12.61 \text{ gms.} \end{array} \qquad \begin{array}{l} 2)253.84 \\ 10)126.92 \\ \hline 12.692 \text{ gms. or 1000 mils } \frac{N}{10} \text{ iodin V.S.} \end{array}$$

Thus each mil of the standard solution represents 0.01261 gm. of crystallized sodium sulphite.

If 1 gm. of the salt is taken, to find the percentage multiply the factor by the number of mils of standard solution consumed, and the result by 100.

Potassium Sulphite ($K_2SO_3 + 2H_2O = 194.37$). Operate upon 0.5 gm. in the same manner as for sodium sulphite.

$$\underbrace{K_2SO_3 + 2H_2O}_{} + I_2 = 2HI + K_2SO_4 + H_2O.$$

$$\begin{array}{l} 2)194.37 \\ 10)\ 97.18 \\ \hline 9.718 \text{ gms. or 1000 mils of standard V.S.} \end{array}$$

Each mil of the $\frac{N}{10}$ iodin represents 0.009718 gm. of crystallized potassium sulphite.

Sodium Bisulphite ($NaHSO_4 = 104.08$). Operate upon about 0.25 gm. in the same manner as for sodium sulphite, and apply the following equation:

$$NaHSO_3 + I_2 + H_2O = 2HI + NaHSO_4.$$

Sodium Thiosulphate (Sodium Hyposulphite) ($Na_2S_2O_3 + 5H_2O = 248.24$). This salt, when brought in contact with iodin, is converted into sodium iodid and sodium tetrathionate. The reaction is expressed by the equation

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

It is estimated as follows: 1 gm. of the salt is dissolved

in 20 mils of water, a few drops of starch solution are added, and then the $\frac{N}{10}$ iodin is delivered in from a burette, until the appearance of blue starch iodid indicates an excess of iodin.

Hydrogen Sulphid ($H_2S = 34.07$). When iodin and hydrogen sulphid are brought together in solution the following reaction occurs:

$$H_2S + 2I = 2HI + S.$$

The reaction is not regular, however, when performed in an acid solution, but in the presence of alkali bicarbonates the results are constant. The method may be employed for the estimation of alkali sulphates.

The process may be conducted as follows:

Into 30 mils of a cold saturated solution of sodium bicarbonate, contained in a 500-mil flask, measure a suitable quantity of the solution of hydrogen sulphid, stopper the flask and mix contents by shaking. Dilute the solution with about 300 mils of water, add starch solution and titrate with $\frac{N}{10}$ iodin V.S. until a distinct and permanent blue color appears.

Each mil of $\frac{N}{10}$ iodin represents 0.0017035 gm. of H_2S.

The residual method may also be employed. A suitable volume of the sample is added to an excess of $\frac{N}{10}$ iodin V.S. mixed with some sodium bicarbonate solution, the solution is thoroughly shaken, and then titrated with $\frac{N}{10}$ thiosulphate; the quantity of the latter, deducted from the quantity of $\frac{N}{10}$ iodin

added, gives the quantity of $\frac{N}{10}$ iodin which reacted with the H_2S.

Sulphids. Soluble sulphids may be estimated by either of the above methods. The solution of sulphid containing about 0.2 gm. being treated like an H_2S solution.

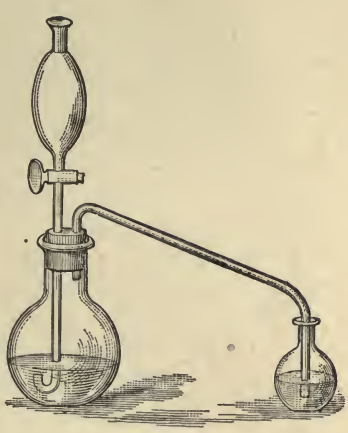

Fig. 47.

Sulphids insoluble in water but decomposable by dilute acids may be estimated as follows:

A weighed quantity of the sulphid is introduced into a flask, provided with a double perforated stopper; through one of the perforations the stem of a separatory funnel is passed, through the other a glass delivery tube (see Fig. 47). The funnel tube extends nearly to the bottom of the flask and is bent to form a hook, the opening of which is under water. The delivery tube begins at the lower end of the stopper and ends in another flask containing sodium bicarbonate solution. The funnel contains diluted sulphuric acid, which, upon opening the glass stop-cock, is allowed to flow into the flask, upon the contained sulphid; the H_2S liberated is conducted into the solution of sodium bicarbonate which absorbs it completely. A current of air aspirated through the apparatus insures absorption of the entire H_2S developed. The sodium bicarbonate solution of H_2S is then titrated with the standard iodin, in the presence of starch.

TABLE OF SUBSTANCES WHICH MAY BE ESTIMATED BY MEANS OF STANDARD IODIN SOLUTION

Name.	Formula.	Molecular Weight.	$\frac{N}{10}$ Factor.
Acid, sulphurous	H_2SO_4	82.09	0.004103
Antimonous oxid	Sb_2O_3	288.4	0.00721
Antimony and potas'm tartrate	$2[K(SbO)C_4H_6O_6]+H_2O$	664.7	0.016617
Arsenous iodid	AsI_3	455.72	0.022786
" oxid	As_2O_3	197.92	0.004948
Cyanogen	CN	26.01	0.0013005
Hydrogen sulphid	H_2S	34.09	0.0017035
Iron (metallic)	Fe_2	111.68	0.002791
Mercuric chlorid	$HgCl_2$	271.52	0.027092
Mercurous chlorid	HgCl	236.06	0.023546
Potassium cyanid	KCN	65.11	0.003255
" sulphite (anhydrous)	K_2SO_3	158.27	0.007913
" (crystallized)	$K_2SO_3+2H_2O$	194.30	0.009718
Sodium bisulphite	$NaHSO_3$	104.08	0.005204
" sulphite (anhydrous)	Na_2SO_3	126.07	0.006303
" " (crystallized)	$Na_2SO_3+7H_2O$	252.18	0.01261
" thiosulphate	$Na_2S_2O_3+5H_2O$	248.22	0.024824
Sulphur dioxid	SO_2	64.07	0.0032035
Tin in stannous compounds	Sn_2	238.0	0.00595
Zinc	Zn_2	130.74	0.003268

Estimation of Substances Readily Reduced.

Any substance which readily yields oxygen in a definite quantity, or is susceptible of an equivalent action, which involves its reduction to a lower quantivalence, may be quantitatively tested by ascertaining how much of a reducing agent of known power is required by a given quantity of the substance for its complete reduction.

The principal reducing agents which may be employed in volumetric analysis are *sodium thiosulphate*, sulphurous acid, arsenous acid, oxalic acid, metallic zinc, and magnesium.

The sodium thiosulphate is the only one which is employed officially in the U. S. P. in the form of a volumetric solution.

It is used in the estimation of free iodin, and indirectly of other free halogens, or compounds in which the halogen is easily liberated, as in the hypochlorites, etc.

Estimations Involving the Use of Sodium Thiosulphate V.S.

(Iodometry)

When sodium thiosulphate acts upon iodin, sodium tetrathionate and sodium iodid are formed, and the solution is decolorized.

This reaction takes place in definite proportions: one molecular weight of the thiosulphate absorbs one atomic weight of iodin.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Chlorin cannot be directly titrated with the thiosulphate, but by adding to the solution containing free chlorin an excess of potassium iodid, the iodin is liberated in exact proportion to the quantity of chlorin present, atom for atom.

$$Cl_2 + 2KI = 2KCl + I_2.$$

Then by estimating the iodin, the quantity of chlorin is ascertained. All bodies which contain available chlorin or bromin, or which when treated with an acid evolve chlorin or bromin, may be estimated by this method.

Also, bodies which contain *available oxygen*, and which when boiled with hydrochloric acid evolve chlorin, such as *manganates*, *chromates*, *peroxids*, etc., may be estimated in this way.

Solutions of *ferric salts*, when acidulated and boiled with an excess of potassium iodid, liberate iodin in exact proportion to the quantity of ferric iron present.

Arsenates, copper salts, and others also liberate iodin from potassium iodid, quantitatively.

Thus sodium thiosulphate may be used in the estimation of a great variety of substances with extreme accuracy.

Preparation of Decinormal Sodium Thiosulphate (Hyposulphite) ($Na_2S_2O_3 + 5H_2O = 248.22$; contains 24.822 gms. in 1 liter). Sodium thiosulphate is a salt of thiosulphuric acid in which two atoms of hydrogen have been replaced by sodium; it therefore seems that a normal solution of this salt should contain one-half the molecular weight in grams in one liter.

But this salt is used chiefly for the estimation of iodin, and, as stated before, one full molecular weight reacts with and decolorizes one atomic weight of iodin, and since one atom of iodin is chemically equivalent to one atom of hydrogen, a full molecular weight of sodium thiosulphate must be contained in a liter of its normal solution.

Sodium thiosulphate is easily obtained in a pure state, and therefore the proper weight of the salt, reduced to powder and dried between sheets of blotting-paper, may be dissolved directly in water, and made up to one liter.

A stronger solution than decinormal is usually made, its titer found, and then the solution diluted to the proper measure.

Thirty gms. of selected crystals of the salt are dissolved in enough water to make, at or near 25° C., 1000 mils.

This concentrated solution is then standardized by one of the following methods:

a. Standardization by Means of $\frac{N}{10}$ *Iodin.* Transfer 10 mils of this solution into a flask or beaker, add a few drops of starch T.S., and then gradually deliver into it from a burette decinormal iodin solution, in small portions at a time, shaking the flask after each addition, and regulating the flow to drops toward the end of the operation. As soon as a blue color is

produced which does not disappear upon shaking, but is not deeper than pale blue, the reaction is completed. Note the number of mils of iodin solution used, and then dilute the thiosulphate solution so that equal volumes of it and the decinormal iodin will exactly correspond to each other, under the above-mentioned conditions.

Example. The 10 mils of sodium thiosulphate, we will assume, require 10.7 mils of decinormal iodin.

The sodium-thiosulphate solution must then be diluted in the proportion of 10 mils to 10.7 mils, or 1000 mils to 1070 mils.

After the solution is thus diluted a new trial should be made, in the manner above described, in which 50 mils of the thiosulphate solution should require exactly 50 mils of the decinormal iodin to produce a faint blue color.

The solution should be kept in small dark amber-colored, glass-stoppered bottles, carefully protected from dust, air, and light.

One mil of this solution is the equivalent of:

Iodin	0.012692	gram.
Bromin	0.007992	"
Chlorin	0.003546	"
Iron in ferric salts	0.005584	"

b. ***Standardization by Means of Potassium Dichromate.*** The potassium dichromate should be pure, if not it should be purified by triple recrystallization and then heated in a porcelain crucible until the entire mass is just fused; then set aside to cool in a desiccator over calcium chlorid or sulphuric acid. The mass falls to a crystalline powder. Of this purified potassium dichromate, weigh off a definite quantity, say 0.2 gm., dissolve it in a small quantity of water, and pour the solution into a beaker containing 2 gms. of pure potassium

iodid (free from iodate) and 100 mils of water. Acidulate the solution with 5 mils of concentrated hydrochloric or sulphuric acid, cover the beaker, and let stand for about five minutes, then titrate with the thiosulphate solution to be standardized (using starch as an indicator) until the blue color is just discharged. The calculation is then made as follows:

$$\underset{294.4}{K_2Cr_2O_7} + \underset{996.12}{6KI} + 14HCl = 2CrCl_3 + 8KCl + 7H_2O + \underset{761.52}{3I_2}.$$

Thus 294.4 gms. of potassium dichromate oxidizes 996.12 gms. of potassium iodid and liberates therefrom 761.52 gms. of iodin.

The potassium iodid must be in excess; in fact for each atom of iodin liberated one molecule of potassium iodid must be present at the completion of the reaction in order to keep the iodin in solution, and thus prevent loss by volatilization.

If 294.4 gms. of potassium dichromate liberate 761.52 gms. of iodin, 0.2 gm. will liberate

$$\frac{761.52 \times 0.2}{294.4} = 0.5173 \text{ gm. of iodin.}$$

$$0.012692 \text{ gm. of iodin} = 1 \text{ mil of } \frac{N}{10} \text{ thiosulphate.}$$

$$0.5173 \quad \text{“} \quad \text{“} \quad \text{“} \quad = 40.172 \text{ mils of } \frac{N}{10} \text{ thiosulphate.}$$

Therefore if in the above assay 37.60 mils of the thiosulphate V.S. were consumed, it must be diluted so that each 37.60 mils will measure 40.72 mils in order to convert the thiosulphate solution into a true decinormal solution. A new trial should then be made with the diluted solution to see if its strength is correct.

It is usually more convenient to use a decinormal dichro-

mate V.S. for standardizing decinormal thiosulphate V.S. This may be done as follows:

Dissolve two grams of pure potassium iodid in a small quantity (10 to 15 mils) of sulphuric acid (1–10). Place this into a 500-mil flask and add to it very slowly 25 mils (accurately measured) of decinormal potassium dichromate V.S., mix well and let stand for five minutes, the flask being kept closed. The thiosulphate solution to be standardized is then run in from a burette in small portions, shaking after each addition until the solution is a pale yellow color. Two mils of starch solution are then added and the titration continued drop by drop until the blue color of starch iodid is just discharged.

Several trials are made, and from an average of three or four closely agreeing results the quantity of water required for dilution to decinormal strength is readily calculated.

Example. Assuming that in the above trial 23.8 mils of the thiosulphate solution were required to react with the iodin liberated by 25 mils of decinormal dichromate, then the thiosulphate must be diluted with distilled water so that each 23.8 mils will measure 25 mils. After dilution a new trial should be made, in which 25 mils of decinormal dichromate should require when treated as above described exactly 25 mils of the thiosulphate.

c. Standardization by Means of Potassium Bi-iodate. This method depends upon the fact that when potassium iodid and bi-iodate are brought together in the presence of a small quantity of an acid, an equivalent amount of iodin is set free. The reaction is illustrated by the equation:

$$\underset{\substack{12)389.94\\10)32.495\\3.2495\text{ gms.}}}{KH(IO_3)_2} + 10KI + 11HCl = \underset{\substack{12)1523.04\\10)126.92\\12.692\text{ gms. or 1000 mils }\frac{N}{10}\text{ V.S.}}}{12I} + 11KCl + 6H_2O.$$

Thus it is seen that one molecule of the bi-iodate causes the liberation of 12 atoms of iodin, against which the thiosulphate solution is standardized.

In order not to use up too large a quantity of the thiosulphate solution in the titration, a very small quantity of the bi-iodate must be taken, and since a small error in weighing this would entail a relatively large error in the results it is best to use the bi-iodate in the form of a solution of known strength and thus obviate the difficulty.

A decinormal solution of the bi-iodate, i.e., one containing in 1000 mils 3.2245 gms. of the salt may be used to advantage. Such a solution will keep unchanged for years, and may be employed as follows for the standardization of sodium thiosulphate solution:

Into a glass-stoppered flask of 250 mils capacity introduce 10 mils of a 5 per cent solution of potassium iodid,* 1 mil of diluted hydrochloric acid and exactly 25 mils of the above potassium bi-iodate solution.

This brownish-yellow solution is now titrated with the sodium thiosulphate solution which is slowly delivered from a burette until the solution becomes pale yellow in color; a few drops of starch solution are now added, and the titration continued (the flow being reduced to drops) until the blue color is just discharged. During the titration, the flask should be frequently stoppered and vigorously shaken.

When the blue color is discharged, note the number of mils used. If an exactly decinormal thiosulphate solution is taken, 25 mils will be required to react with the 25 mils of potassium bi-iodate solution, under the above conditions. If,

* The potassium iodid must be in sufficient quantity not only to react with the bi-iodate quantitatively, as shown in the equation, but also to dissolve the iodin which is liberated.

on the other hand, only 22 mils of the thiosulphate solution are used in the titration, then the latter is too strong, and must be diluted so that each 22 mils will measure 25 mils in order to make it strictly decinormal.

d. Standardization by Means of Potassium Permanganate. Sodium thiosulphate solution may be accurately standardized by means of potassium permanganate, if the other substances used for this purpose are not at hand. The method is easily understood by referring to the iodometric standardization of potassium permanganate solution. See page 145.

Estimation of Free Iodin (I = 126.92). Iodin in the dry state or in the form of a tincture is brought into aqueous solution by means of pure potassium iodid and then titrated with standard sodium thiosulphate. The potassium iodid is used here to dissolve the iodin; it must be free from iodate (KIO_3) because the presence of this salt would cause a liberation of iodin from the potassium iodid.

Dry iodin is assayed as follows:

About 0.5 gm. of iodin are placed in a tightly stoppered weighing bottle and accurately weighed. One gram of potassium iodid and 50 mils of water are added, and when the iodin is dissolved, $\frac{N}{10}$ sodium thiosulphate is delivered from a burette in small portions at a time, shaking after each addition until the reaction is nearly completed, and the solution is of a faint yellow color. A few drops of starch indicator are now added, and the titration with the thiosulphate continued drop by drop until a final drop just discharges the blue color. The number of mils of the thiosulphate solution used is noted. This number, multiplied by the decinormal factor for iodin, gives the weight of the latter present in the sample assayed.

$$I_2 + 2(Na_2S_2O_3 + 5H_2O) = Na_2S_4O_6 + 2NaI + 10H_2O.$$

$2)253.84$ $\quad$ $2)496.96$

$10)126.92$ $\quad$ $10)248.48$

12.692 gms. $\quad$ 24.848 gms. or 1000 mils $\frac{N}{10}$ V.S.

Each mil of $\frac{N}{10}$ thiosulphate represents 0.012692 gm. of iodin.

If in the above assay 39 mils of $\frac{N}{10}$ sodium thiosulphate were consumed, then

$$0.012692 \times 39 = 0.495 \text{ gm.}$$

$$\frac{0.495 + 100}{0.5} = 99 \text{ per cent.}$$

Lugol's Solution. This is an aqueous solution of iodin and potassium iodid.

It is estimated for iodin in the same way as the foregoing. The potassium iodid acts merely as a solvent for free iodin, and does not enter into the reaction.

Ten or twelve grams of the solution is a convenient quantity to operate upon. Starch solution is the indicator.

Tincture of Iodin. An alcoholic solution of free iodin must be diluted with a solution of potassium iodid, before titration, in order to prevent the precipitation of iodin, which would result upon the addition of the aqueous standard solution. The U.S.P. tincture of iodin contains potassium iodid and therefore may be titrated as it is.

Indirect Iodometric Estimations. The titration methods previously described, in which iodin is used as a standard solution and the estimation of free iodin by means of sodium thiosulphate, are classed as *direct iodometric methods*. The following methods, in which the strength of the substance under analysis is determined by the quantity of iodin which

it liberates from an iodid, are known as *indirect iodometric methods*. Potassium iodid is added in excess * to an acidulated solution of the substance, and the liberated iodin estimated by means of standard thiosulphate. These methods are among the most accurate of all volumetric analyses, and take in a very large class of substances. Among the substances which may be analyzed by this method are chlorin and bromin and all substances which readily liberate these elements: ferric salts, manganates, chromates, metallic peroxids, and other substances from which oxygen can be easily liberated.

Free Chlorin or Bromin. Free chlorin acts upon potassium iodid, liberating iodin, as per the equation

$$Cl_2 + 2KI = 2KCl + I_2.$$

Thus it is seen that each atom of chlorin will liberate one atom of iodin, hence by determining the quantity of iodin by means of a standard thiosulphate solution the quantity of chlorin present is easily ascertained (126.92 gms. of I = 35.46 gms. of Cl). The same applies to free bromin, one atom of bromin (79.92) will liberate one atom of iodin (126.92) $Br_2 + 2KI = 2KBr + I_2$. 1000 mils of $\frac{N}{10}$ sodium thiosulphate is equivalent to 12.692 gms. of iodin, and hence to 3.546 gms. of chlorin or 7.992 gms. of bromin.

Thus 1 mil of $\frac{N}{10}$ sodium thiosulphate is equivalent to 0.012692 gm. of iodin; 0.003546 gm. of chlorin; 0.007992 gm. of bromin.

Chlorin cannot be directly titrated with sodium thiosul-

* The iodid should be in sufficient excess to keep the liberated iodin in solution as KI.I.

phate because, instead of the tetrathionate being formed as with iodin, sulphuric acid is produced; furthermore there is no readily observable end-point as there is with iodin.

Chlorin Water. This is an aqueous solution of chlorin, Cl = 35.46, containing at least 0.4 per cent of the gas.

The estimation of chlorin is effected in an indirect way, namely, by determining the quantity of iodin which it liberates from potassium iodid.

A definite quantity of chlorin will liberate a definite quantity of iodin from an iodid; these quantities are in exact proportion to their atomic weights, as the equation shows:

$$\underset{\substack{2)70.92\\10)35.46\\3.546}}{Cl_2} + 2KI = 2KCl + \underset{\substack{2)253.84\\10)126.92\\12.692 \text{ gms.}}}{I_2}.$$

Thus it is seen that by estimating the liberated iodin the quantity of chlorin may be determined with accuracy.

Ten grams is a convenient quantity to operate upon. To this about half a gram of potassium iodid is added. A little starch solution is then introduced, and the titration is begun with decinormal sodium thiosulphate.

When the blue color of starch iodid has entirely disappeared the reaction is finished.

The reaction between iodin and sodium thiosulphate is illustrated by the following equation:

$$\underset{\substack{2)253.84\\10)126.92\\12.692 \text{ gms.}}}{I_2} + 2\underset{\substack{2)496.96\\10)248.48\\24.848 \text{ gms. or } 1000 \text{ mils } \frac{N}{10} \text{ V.S.}}}{(Na_2S_2O_3 + 5H_2O)} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

Thus we see that 1000 mils of $\frac{N}{10}$ $Na_2S_2O_3 . 5H_2O$ represent

12.692 gms. of iodin, which are equivalent to 3.546 gms. of chlorin.

Each mil therefore is equivalent to 0.003518 gm. of chlorin. This number is the factor which, when multiplied by the number of mils of $\frac{N}{10}$ thiosulphate used, gives the weight in grams of chlorin contained in the quantity of chlorin water acted upon.

Chlorinated Lime (Calx Chlorinata, Chlorid of Lime, Bleaching-powder). This substance was formerly supposed to be a compound of lime and chlorin, $CaOCl_2$, and hence the name chlorid of lime. It is now generally considered to be a mixture principally of calcium chlorid and calcium hypochlorite, $CaCl_2 + Ca(ClO)_2$ or $Ca(OCl)Cl$. The hypochlorite is the active constituent. This is a very unstable salt, and is readily decomposed even by carbonic acid. When treated with hydrochloric acid it gives off chlorin.

The value of chlorinated lime as a bleaching or disinfecting agent depends upon its available chlorin, that is, the chlorin which the hypochlorite yields when treated with an acid.

In estimating the available chlorin, the latter is liberated with acetic acid. This liberated gas, then, acting upon potassium iodid, sets free an equivalent amount of iodin. The quantity of iodin is then determined, and thus the amount of available chlorin found. 0.2 to 0.4 gm. are convenient quantities to operate upon.

Introduce into a stoppered weighing bottle between 3 and 4 gms. of chlorinated lime and weigh accurately. (In order to make the descriptions simpler we will assume that 3.5 gms. is the weight taken.) This is triturated thoroughly with 50 mils of water, and the mixture transferred to a graduated vessel, together with the rinsings, and made up to 1000 mils with water. This is thoroughly shaken, 100 mils of it (repre-

senting 0.35 gm. of the sample) are removed by means of a pipette and treated with 1 gm. of potassium iodid * and 5 mils of acetic acid, and into the resulting reddish-brown liquid the $\frac{N}{10}$ sodium thiosulphate is delivered from a burette. Towards the end of the titration, when the brownish color of the liquid is very faint, a few drops of starch solution are added and the titration continued until the bluish or greenish color produced by the starch has entirely disappeared. Not less than 30 mils of the volumetric solution sould be required to produce this result.

The reactions which take place in this process are illustrated by the following equations:

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2$$

or $$Ca(OCl)Cl + 2HC_2H_3O_2 = Ca(C_2H_3O_2)_2 + H_2O + Cl_2,$$

$$Cl_2 + 2KI = 2KCl + I_2.$$

$$\begin{array}{r} 2)70.92 \\ 10)35.46 \\ \hline 3.546 \text{ gms.} \end{array} \qquad \begin{array}{r} 2)253.84 \\ 10)126.92 \\ \hline 12.692 \text{ gms.} \end{array}$$

$$I_2 + 2(Na_2S_2O_3 + 5H_2O) = 2NaI + Na_2S_4O_6 + 10H_2O.$$

$$\begin{array}{r} 2)253.84 \\ 10)126.92 \\ \hline 12.692 \text{ gms.} \end{array} = 1000 \text{ mils } \frac{N}{10} \text{ thiosulphate V.S.}$$

It is thus seen that 1 mil of the decinormal sodium thiosulphate represents 0.012692 gm. of iodin, which in turn is equivalent to 0.003546 gm. of chlorin.

Then

$$0.003546 \times 30 = 0.1063 \text{ gm.}$$

$$\frac{0.1063 \times 100}{0.35} = 30.37 \text{ per cent of available chlorin.}$$

* In order to assume a sufficient excess of potassium iodid, take twice as much of it as of the bleaching-powder.

This is a very rapid method for estimating chlorin; but when calcium chlorate is present in the bleaching-powder (and it often is, through imperfect manufacture) the chlorin from it is recorded, as well as that from the hypochlorite, the chlorate being decomposed into chlorin, etc., by hydrochloric acid (which is sometimes used). The chlorate, however, is of no value in bleaching; its chlorin is not available. Hence, unless the powder is known to be free from chlorate, the analysis should be made by means of arsenous-acid solution, or by using acetic acid instead of hydrochloric, and thus avoid liberating chlorin from the chlorate which may be present.

The various bleaching preparations of the market which depend upon their available chlorin are all salts of hypochlorous acid (HClO) or solutions of such salts.

Eau de Javelle (Javelle's Water) is a solution of potassium hypochlorite and potassium chlorid. A solution of magnesium hypochlorite is known in commerce as *Ramsay's* or *Grouvelle's Bleaching Fluid.* The solution known as *Wilson's Bleaching Fluid* contains aluminum hypochlorite.

Solution of Chlorinated Soda (Labarraque's Solution). This is an aqueous solution of several chlorin compounds of sodium, principally sodium chlorid and hypochlorite, containing at least 2.4 per cent by weight of available chlorin.

In this solution, as in chlorinated lime, it is the available chlorin which is estimated. The chlorin is first liberated with hydrochloric or acetic acid; this then liberates iodin from potassium iodid, and the free iodin is then determined by standard sodium thiosulphate.

Seven grams of chlorinated soda solution are mixed with 50 mils of water, 2 gms. of potassium iodid, and 10 mils of acetic acid are then added, together with a few drops of starch solution. Into this mixture the decinormal sodium thiosulphate is delivered from a burette until the blue or greenish

tint of the liquid is just discharged. Each mil of $\frac{N}{10}$ thiosulphate used up represents 0.003546 gm. of available chlorin. The potassium iodid should always be added before the acetic acid, so that the chlorin has potassium iodid to act upon as it is liberated, and thus loss of chlorin is obviated.

Bromin Water, or any substance containing free bromin may be assayed in exactly the same manner as that described for chlorin water. Free chlorin must, however, be absent.

Each mil of $\frac{N}{10}$ thiosulphate solution represents 0.007992 gm. of bromin.

Assay of Hydrogen Dioxid ($H_2O_2 = 34$). The iodometric method, which originated with Kingzett,* is based upon the fact that iodin is liberated from potassium iodid by hydrogen dioxid, in the presence of sulphuric acid, and that this liberation of iodin is in direct proportion to the available oxygen contained in the dioxid.

Then by determining the amount of iodin liberated, the available oxygen is readily found.

$$\underset{2)34}{H_2O_2} + H_2SO_4 + 2KI = K_2SO_4 + \underset{2)16}{2H_2O} + \underset{2)253.84}{I_2}.$$

$$\underset{17 = 1 \text{ available O} =}{} \qquad \underset{8}{} \qquad \underset{126.92}{}$$

This shows that 126.92 gms. of iodin are liberated by 17 gms. of absolute dioxid, which are equivalent to 8 gms. of available oxygen.

Thus 1000 mils of $\frac{N}{10}$ sodium thiosulphate V.S., which absorb and consequently represent 12.692 gms. of iodin, are equivalent to 1.7 gms. of H_2O_2 or 0.8 gm. of available oxygen.

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* J. Chem. Soc., 1880, Vol. 37, p. 792.

Each mil of this $\frac{N}{10}$ V.S., then, represents 0.0017 gm. of H_2O_2, and 0.0008 gm. of available oxygen.

The coefficients for weight of H_2O_2 and of oxygen, it is seen, are identical with those used in the permanganate process. Therefore the coefficient for volume is also the same in this method as in the other if 1 mil be taken for assay.

The process is carried out as follows: Take 2 or 3 mils of sulphuric acid, dilute it with about 30 mils of water, add an excess of potassium iodid (about 1 gm.), and then 1 mil of hydrogen dioxid. After the mixture has been allowed to stand five minutes, starch solution * is added, and the titration with $\frac{N}{10}$ sodium thiosulphate begun.

Note the number of mils required to discharge the blue color, and multiply this number: by 0.0017 gm. to find the quantity, by weight, of H_2O_2; by 0.0008 gm. to find the weight of available oxygen; by 0.57 mil to find the volume of available oxygen.

If 18 mils are required, the solution is of $0.57 \times 18 = 10.26$ volume strength.

$0.0017 \times 18 = 0.0306$ or 3.06 per cent H_2O_2.

$0.0008 \times 18 = 0.0144$ or 1.44 per cent of oxygen.

With this method the author has always obtained satisfactory results. The lack of uniformity in the reaction, which is frequently reported, is doubtless due to the use of insufficient acid or to taking a too concentrated solution of the dioxid.

The best results are obtained if the solution is not more than two volumes strength.

* Starch solution may be omitted, as the decolorization of the iodin is distinctly seen if the beaker is placed upon a white surface.

The sulphuric acid used in this assay must be free from sulphurous acid, arsenous acid and nitric acid, and the potassium iodid must contain no iodate.

Distillation Methods. Manganates, chromates, metallic peroxids, and a great variety of substances containing oxygen, including antimonic oxid and arsenic pentoxid, will, when heated with concentrated hydrochloric, liberate an equivalent amount of chlorin. This is illustrated by the following equation:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The chlorin which is evolved, is passed into a solution of potassium iodid and liberates an equivalent of iodin, which latter substance is then estimated by titration with sodium thiosulphate solution. The quantity so found is therefore a measure of the original substance and of its oxygen content. The process may be carried out by means of the apparatus

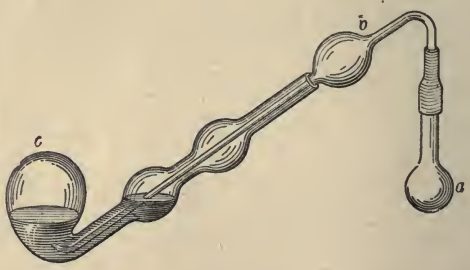


Fig. 48.

devised by Bunsen, Fig. 48, or by that of Fresenius, Fig. 49, or Mohr, Fig. 50.

An accurately weighed quantity of the substance to be analyzed is introduced into the round-bottomed flask *a*, Fig. 48. The flask is then filled to about two-thirds its capacity with concentrated hydrochloric acid, and quickly connected by means of a short rubber tube with a long-bulbed delivery

tube, *b*, which is introduced into and extends to the bottom of an inverted bulbed retort, *c*. The larger bulb of the retort is filled to two-thirds of its capacity with a 10 per cent solution of potassium iodid. Heat is applied to the flask, and the chlorin distils over into the potassium iodid solution, which becomes brownish-red through liberation of iodin. The distillation is continued until about one-third of the acid fluid has passed over or until a peculiar cracking sound indicates the absorption of hot hydrochloric acid vapor.

The flask, together with its delivery tube, is then slowly removed, the heating, however, is continued until the tube

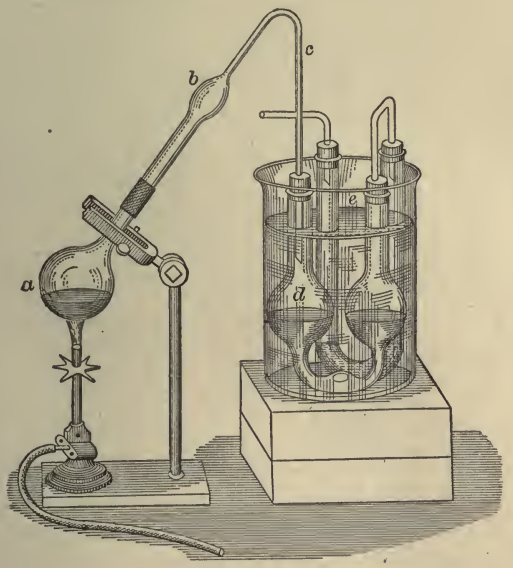


FIG. 49.

is entirely withdrawn, in order to prevent the iodid solution being drawn over into the flask. The retort is then shaken so that any traces of chlorin which may have escaped absorption, are taken up and the contents of the retort poured into

a beaker; the retort and the delivery tube are then rinsed with water and the rinsings added to the fluid in the beaker, and titration with standard sodium thiosulphate begun immediately.

It is important that the quantity of potassium iodid is sufficient to keep the liberated iodin in solution, and the potassium iodid free from iodate, and the titration started without delay to avoid liberation of iodin through action of the air upon the strongly acid potassium iodid solution. When all the chlorin has passed over and hydrochloric acid gas begins to distil, the liquid in the retort is apt to be drawn back into the flask because of the great affinity which hydrochloric acid gas has for water, and the resultant condensation in the flask. This regurgitation may be avoided by introducing into the generating flask a small piece of magnesite, which slowly dissolves in the acid solution and so keeps up a constant flow of carbon dioxid, which by its pressure prevents back-flow of the fluid. The bulbs in the retort and delivery tube are also calculated to prevent this regurgitation.

The Fresenius apparatus is illustrated in Fig. 49. In this the potassium iodid solution is contained in two joined U-shaped tubes. The delivery tube from the distilling flask enters one of the U-tubes through a paraffin-soaked cork (which fits tightly), and terminates just above the potassium iodid solution. In operation the U-tubes should be kept in ice water, and all the fittings should be air-tight. Paraffin-covered cork stoppers only should be used.

After all the chlorin has passed over or when about one-third of the acid has distilled over, the apparatus is allowed to stand for a few minutes, to permit all traces of chlorin to become absorbed; the application of a suction pump to the rear outlet tube will help to bring about this result.

Mohr's apparatus, shown in Fig. 50, is of very simple construction and easy to use.

The distilling flask is fitted with a paraffin-soaked cork, through which a delivery tube containing one bulb passes; this delivery tube again passes through a common cork which loosely fits a stout, large test tube, containing the potassium iodid solution. The delivery tube is drawn out to a fine point and reaches to near the bottom of the test tube. The latter is placed, when in operation, in a hydrometer jar containing cold water.

Estimation of Manganese Dioxid ($MnO_2 = 86.93$). 0.4 gm. of pulverized manganese dioxid is placed into the distil-

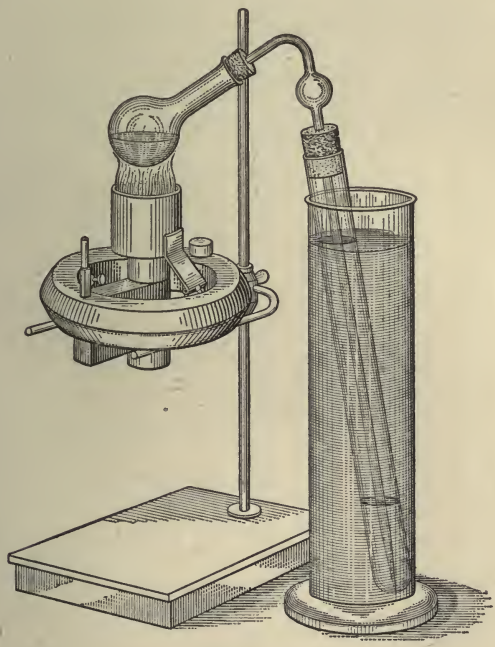


Fig. 50.

ling flask (*a*, Fig. 48 or Fig. 49) and the latter filled to two-thirds of its capacity with concentrated hydrochloric acid and

connected without delay with the vessel containing the potassium iodid solution. The flask is then gradually heated so that a steady current of chlorin passes over into the potassium iodid solution. When the evolution of chlorin gas begins to diminish, the heat is slowly raised to boiling, and continued at this point until about one-third of the acid liquid has distilled over. The delivery tube is then removed and rinsed, as previously described, and the liberated iodin titrated by means of $\frac{N}{10}$ sodium thiosulphate solution, of which we will assume 60 mils were consumed.

The reactions are as follows:

(*a*) $$\underset{86.93}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{70.92}{Cl_2}.$$

(*b*) $$\underset{70.92}{Cl_2} + 2KI = 2KCl + \underset{253.84}{I_2}.$$

(*c*) $$\underset{2)253.84}{\underset{10)126.92}{I_2}} + \underset{2)496.96}{\underset{10)248.48}{2Na_2S_2O_3 \cdot 5H_2O}} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

12.692 gms. 24.848 gms. = 1000 mils $\frac{N}{10}$ V.S.

0.012692 gm. = 1 mil $\frac{N}{10}$ V.S.

These equations show that 494.96 gms. of sodium thiosulphate will decolorize 253.84 gms. of iodin, which quantity is liberated by 70.92 gms. of chlorin, which is itself liberated from hydrochloric acid by 86.93 gms. of manganese dioxid.

Therefore 1 mil of a decinormal solution of sodium thiosulphate (containing 24.848 gms. in 1000 mils) is equivalent to 0.012692 gm. of I; 0.003546 gm. of Cl; 0.0043465 gm. of MnO_2; 0.0008 gm. of O (available).

The 60 mils of the thiosulphate solution used in this assay will therefore represent $0.0043465 \times 60 = 0.2608$ gm. of pure MnO_2, or 65.2 per cent.

$$\frac{0.2608 \times 100}{0.4} = 65.2 \text{ per cent.}$$

This is the method which should be used for the assay of native manganese dioxid. The freshly precipitated manganese dioxid of the Pharmacopœia may be assayed by the more easily performed digestion method described on page 233.

Estimation of Chromic Acid and Chromates. Chromic anhydrid, chromium trioxid ($CrO_3 = 100$), when heated with concentrated hydrochloric acid, liberates chlorin as per the equation,

$$\underset{100}{CrO_3} + 6HCl = CrCl_3 + 3H_2O + \underset{3\times35.46}{Cl_3}.$$

One hundred parts of CrO_3 liberates 3×35.46 parts of Cl, hence one atomic weight of chlorin, 35.46 parts, represents 33.3 +parts of CrO_3. Or 1 mil of $\frac{N}{10}$ sodium thiosulphate represents 0.00333 gm. of CrO_3.

Estimation of Potassium Dichromate ($K_2Cr_2O_7 = 294.20$). This salt, as explained in a previous chapter, has three atoms of oxygen available for oxidation. A molecule of this salt is therefore equivalent to six atoms of chlorin, and when boiled with hydrochloric acid will liberate six atoms of chlorin, as the equation shows.

$$\underset{294.2}{K_2Cr_2O_7} + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + \underset{6\times35.46}{3Cl_2}.$$

Thus one atom of liberated chlorin will represent one-sixth of 294.2, which is 49.03 + parts of potassium dichromate. Then 1 mil of $\frac{N}{10}$ sodium thiosulphate will represent 0.004903 gm. of $K_2Cr_2O_7$. In the same way all other chromates may be treated, but these compounds will, when treated with hydrochloric acid, liberate chlorin at once and without the applica-

tion of much heat, hence some chlorin is apt to be lost before the distillation flask can be connected with the apparatus, and therefore it is more convenient to employ the digestion method later described.

The reaction in the case of neutral potassium chromate is as follows:

$$\underset{194.2}{K_2CrO_4} + 8HCl = 2KCl + 4H_2O + CrCl_3 + Cl_3.$$

Lead peroxid, PbO_2; cobaltic oxid, Co_2O_3; nickel oxid, Ni_2O_3, as well as many other substances, may be assayed by this distillation method.

Estimation of Alkali Iodids by the Distillation Method. This method is based upon the fact that metallic iodids, when

FIG. 51.

treated with ferric salts in acidulated solution, yield up all of their iodin. As shown in the equation

$$Fe_2(SO_4)_3 + 2KI = K_2SO_4 + 2FeSO_4 + I_2.$$

The iodin thus set free is distilled into a solution of potassium iodid and its quantity determined by titration with sodium thiosulphate in the usual manner.

For the reaction, ferric sulphate or ammonio-ferric alum may be used; the latter is, however, preferred because of its paler color. Ferric sulphate and ferric chlorid are so dark in color that the determination of the end-reaction is quite a difficult matter; furthermore, these salts frequently contain traces of nitrates which, if present, liberate chlorin from the chlorids or distil over and liberate iodin from the potassium iodid solution in the receiving vessel. Ferric chlorid is particularly objectionable because of the tenacity with which it holds the last portions of iodin.

The distillation may be done in the Fresenius apparatus, Fig. 49, or better in that shown in Fig. 51. The latter consists of a 100-mils distilling flask (*a*), connected by means of a glass tube with a nitrogen flask (*b*), which contains a 10 per cent potassium iodid solution, and which is kept in a vessel of ice water when in use. The stoppers used are cork, well soaked in paraffin. The construction of the flask is particularly suitable, because it presents a large surface to the vapor of iodin which distils over, and because the titration can be done directly in it, thus avoiding the necessity of transferring its contents to a beaker or other vessel.

The glass tube which conveys the iodin vapor must not be carried into the solution of potassium iodid and must not be drawn to a fine point. The reason for this is that the iodin condensing at the point would soon choke up the tube and prevent the further passage of iodin vapor. Any iodin which condenses in the tube is washed down into the potassium iodid solution by the steam during the distillation.

The Process. Into the flask (*a*) is introduced about 5 gms. of ammonio-ferric alum, 50 mils of water, 20 mils of diluted sulphuric acid (1:10), and the iodid to be examined, accurately weighed. Take about 0.5 gm. The flask is then connected with the receiving vessel (*b*), which is about half filled with a

10 per cent potassium iodid solution, and after connections are made tight, heat is gradually applied to the distilling flask. After most of the iodin has passed over, the heat is raised to boiling, and continued at this temperature until about one-fourth of the liquid has passed over, and the solution in the distilling flask is no longer of a brown color.

When the receiving vessel has sufficiently cooled, it is disconnected and its contents titrated with decinormal sodium thiosulphate, using starch as indicator. Before beginning titration, however, it is necessary to rinse the lower extremity of the tube and the stopper into the solution in the receiving vessel, in order that every trace of iodin be collected.

The calculation is then made as follows:

(*a*) $Fe_2(SO_4)_3.(NH_4)_2SO_4 + 2KI$ (332.04) $= K_2SO_4 + (NH_4)_2SO_4 + 2FeSO_4 + I_2$ (253.84).

(*b*) $I_2 + 2Na_2S_2O_3 + 5H_2O = 2NaI + Na_2S_4O_6 + 10H_2O$.

$2)253.84$

$10)126.92$

12.692 gms. = 1000 mils $\frac{N}{10}$ V.S.

0.012692 gm. = 1 mil $\frac{N}{10}$ V.S.

Referring to the above equations we see that 253.84 gms. of iodin are liberated from 332.04 gms. of potassium iodid; thus 126.92 gms. of iodin represent 166.02 gms. of potassium iodid, and therefore 1 mil of decinormal sodium thiosulphate solution, representing 0.012692 gm. of iodin, will at the same time represent 0.016602 gm. of KI.

If in the above assay 29 mils of $\frac{N}{10}$ sodium thiosulphate are consumed, we multiply the factor for KI = 0.016602 gm. by 29, this gives 0.4814+ gm., the quantity of pure KI in the 0.5 gm. taken, which is about 96 per cent.

Digestion Methods. The distillation methods above described may be avoided in many cases and the more easily performed digestion process used. For instance, freshly precipitated manganese dioxid, lead peroxid, chromic acid, chlorates, bromates, iodates, ferric salts, and a great many other substances, may be assayed by mere digestion with hydrochloric acid at a slightly elevated temperature.

The digestion is performed in a strong glass bottle, provided with an accurately fitting ground-glass stopper which is tied down by means of wire or secured by a clamp. See Fig. 52.

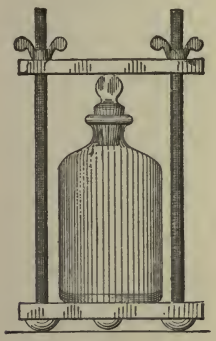


Fig. 52.

Before using the bottle for this operation it should be tested by securely tying down the stopper and immersing the bottle entirely in hot water to see if the stopper fits sufficiently tight. If it does not, bubbles of air will escape from inside, and the bottle is useless for the purpose intended. In that event the stopper must be reground into the neck of the bottle with a little very fine emery and water. The capacity of the bottle may vary from 50 to 150 mils.

The Process. The substance is accurately weighed and introduced into the bottle together with a small quantity of coarsely powdered glass or small pure flint pebbles (to prevent caking, especially in the case of insoluble powders). A sufficient excess of potassium iodid solution is then added, followed by some pure concentrated hydrochloric acid. The stopper is then quickly inserted, firmly secured by wire or a clamp, and the bottle placed in a water bath, and the water gradually heated to boiling; this temperature being continued until decomposition is complete, which is usually in about half an

hour. The bottle is then allowed to cool slowly and its contents emptied into a beaker. Then, after washing the bottle and adding the washings to the contents of the beaker, the liberated iodin is estimated by titration with sodium thiosulphate.

The potassium iodid used in this process must be absolutely free from iodate.

One mil of $\frac{N}{10}$ sodium thiosulphate is equivalent to

$KClO_3$	0.002042	gm.
$NaClO_3$	0.001784	"
$KBrO_3$	0.0027836	"
KIO_3	0.003567	"
MnO_2	0.0043465	"
PbO_2	0.011955	"
CrO_3	0.00333	"

Estimation of Chlorates, Bromates and Iodates. The estimation of these salts is based upon the fact that in each case one equivalent of the acid or its monobasic salt liberates six equivalents of chlorin and consequently six equivalents of iodin when decomposed by the digestion method.

This is illustrated by the equations:

(*a*) $KClO_3 + 6HCl = 3H_2O + KCl + Cl_6$;

(*b*) $KBrO_3 + 6HCl = 3H_2O + KBr + Cl_6$;

(*c*) $KIO_3 + 6HCl = 3H_2O + KI + Cl_6$.

and

(*d*) $Cl_6 + 6KI = 6KCl + I_6$.

In the distillation process, however, bromates and iodates liberate only four equivalents of iodin, while bromous chlorid

and iodous chlorid remain in the retort, therefore in these cases the digestion is preferable to the distillation method.

If the bromate or iodate to be assayed contains any bromid or iodid, bromin or iodin respectively will be liberated upon the addition of the acid, according to the equations

$$(a) \quad 5KBr + KBrO_3 + 6HCl = 6KCl + 3H_2O + Br_6;$$

$$(b) \quad 5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + I_6;$$

therefore the method is not applicable for the assay of such mixtures.

The presence of either of these salts may be ascertained by moistening a small quantity of the salt with dilute sulphuric acid, when if a yellow or brown coloration results, either a bromid or an iodid respectively is present.

Example. Estimation of Potassium Chlorate. 0.2 gm. of the salt is introduced into the digestion bottle of about 100 mils capacity, 10 mils of water added, and about 4 gms. of potassium iodid (or sufficient of its saturated solution). This is followed by 10 mils of concentrated hydrochloric acid, the stopper quickly inserted, firmly secured by wiring or a clamp, and the flask placed, stopper downward, in a water bath. The water is gradually raised to boiling and kept at this temperature for about half an hour. It is then allowed to cool slowly, and the contents of the bottle washed into a beaker and titrated with decinormal sodium thiosulphate, using starch as indicator. The number of mils of $\frac{N}{10}$ thiosulphate solution used, multiplied by 0.002042 gm. gives the weight of pure $KClO_3$ present in the sample.

In the assay of bromates and iodates a smaller quantity of hydrochloric acid may be used, and a lower temperature, say 50° C., is sufficient for decomposition.

Example. Estimation of Potassium Bromate. 0.2 gm. of the salt is dissolved in 15 mils of water, 4 gms. of potassium iodid are added, followed by 4 mils of concentrated hydrochloric acid. The bottle is securely closed, as in the foregoing assay, and heated for half an hour at 50° C. Then, after decomposition, titration with $\frac{N}{10}$ sodium thiosulphate solution is begun, each mil of which represents 0.2836 gm. of pure $KBrO_3$.

If $\frac{1}{1000}$ of one-sixth of the molecular weight of either salt be taken for assay, each mil of the $\frac{N}{10}$ thiosulphate solution used will indicate 1 per cent purity.

Estimation of Ferric Salts. When a ferric salt in an acidulated solution is digested with an excess of potassium iodid, the salt is reduced to the ferrous state, and iodin is set free.

$$Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2.$$

One atom of iodin is liberated for each atom of iron in the ferric state. The liberated iodin is then determined by sodium thiosulphate in the usual way. 126.92 gms. of iodin = 55.82 gms. of metallic iron.

The method is exemplified in the following assay:

Ferric Chlorid (Fe_2Cl_6 or $FeCl_3$). 0.5 of the dry salt accurately weighed is put into a 100-mil glass-stoppered bottle, 15 mils of water are added to dissolve the salt, and then 3 mils of concentrated hydrochloric acid and 2 gms. of pure potassium iodid are introduced. The bottle is securely closed and its contents heated to 40° C. (104° F.) for half an hour. A higher temperature must be avoided, otherwise iodin will be volatilized. The liquid is then cooled and the liberated iodin titrated with $\frac{N}{10}$ sodium thiosulphate until the color is just discharged. Starch may used as indicator.

Each mil of $\frac{N}{10}$ thiosulphate solution used represents 0.005582 gm. of metallic iron or 0.01622 gm. of pure ferric chlorid.

The following equations illustrate the reactions:

$$\underset{2)324.4}{\underset{162.2}{Fe_2Cl_6}} + 2KI = 2FeCl_2 + 2KCl + \underset{2)253.84}{\underset{126.92}{I_2}}.$$

Then

$$\underset{2)253.84}{\underset{10)126.92}{I_2}} + 2Na_2S_2O_3.5H_2O = 2NaI + Na_2S_4O_6 + 10H_2O.$$

12.692 gms. = 1000 mils $\frac{N}{10}$ V.S.

The assay of other ferric salts is practically the same as that described above.

Each mil. of $\frac{N}{10}$ sodium thiosulphate is equivalent to

Ferrum, Fe	0.005582 gm.
Ferric ammonium sulphate, $Fe_2(SO_4)_3.(NH_4)_2SO_4$	0.0266 "
Ferric chlorid, Fe_2Cl_6	0.01622 "
" " (cryst.), $Fe_2Cl_6+12H_2O$	0.02702 "
" nitrate, $Fe_2(NO_3)_6$	0.024185 "
" oxid, Fe_2O_3	0.007982 "
" sulphate, $Fe_2(SO_4)_3$	0.019992 "

In the case of the scale salts of iron, which are mostly of indefinite and variable composition, it is the quantity of metallic iron present which is determined.

The solutions of ferric salts are estimated in the same manner. It is the rule to take 1 to 2 gms. of the solution for assay.

Assay of Chromic Acid, Chromates and Dichromates. Dissolve about 1 gm. of the substances accurately weighed in a stoppered weighing bottle, in sufficient distilled water to measure 100 mils.

To 15 mils of this solution add 3 mils of hydrochloric acid

and 2 gms. of potassium iodid in a glass-stoppered container, shake the mixture, allow it to stand for five minutes, then dilute with distilled water to measure 100 mils, and titrate with tenth-normal sodium thiosulphate V.S., using starch T.S. as indicator.

Each mil of the thiosulphate V.S. used corresponds to 0.00333 gm. of CrO_3.

See equations on page 229.

Assay of Arsenic Oxid (As_2O_5) and Arsenates. *Also antimonic compounds.* Dissolve about 0.5 gm. of the substance accurately weighed in 25 mils of distilled water, heat the solution to 80° C. and add 10 mils of hydrochloric and 3 gms. of potassium iodid. Allow the mixture to stand for fifteen minutes at 80° C., then cool and titrate with tenth-normal sodium thiosulphate V.S., using starch as indicator. The solution must be decidedly acid in reaction. The function of the acid is expressed by the equation

$$KI + HCl = KCl + HI.$$

The HI then reacts with the As_2O_5, reducing it to As_2O_3 and liberating iodin, as the following equation shows:

$$As_2O_5 + 4HI = As_2O_3 + 2H_2O + 2I_2.$$

Each mil of the tenth-normal thiosulphate V.S. corresponds to 0.005748 gm. of As_2O_5 or 0.0092985 gm. of Na_2HAsO_4 (sodium arsenate.)

Assay of Copper. This method depends upon the reaction between copper salt and potassium iodid, in which iodin is quantitatively liberated.

$$\underset{2\times159.64}{2CuSO_4} + 4\,KI = Cu_2I_2 + 2K_2SO_4 + \underset{2\times126.92}{I_2}.$$

The solution of the copper sulphate should be weakly acid. Acetic acid is usually used. All iodin liberating substances

must be absent, as well as all metals which react with iodin, as Pb, As, Sb, Bi, etc.

The Process. About 1 gm. of the copper salt, accurately weighed, is dissolved in 50 mils of distilled water; to this is added 4 mils of acetic acid and 3 gms. of potassium iodid. The liberated iodin is then titrated with tenth-normal sodium thiosulphate V.S., using starch as indicator. Each mil of the thiosulphate V.S. corresponds to 0.006357 gm. metallic copper or 0.015964 gm. of $CuSO_4$.

If copper nitrate is to be assayed, the NO_3 ion must be taken up with ammonia-water, which is added until a clear blue solution results, this is boiled for about one minute, and then acidified with acetic acid, or the solution is evaporated with sulphuric acid until the nitric acid is expelled.

Assay of Mercuric Salt. The mercury is precipitated out of an alkaline solution by formaldehyde, and then dissolved in an excess of standard iodin solution in the presence of potassium iodid. The excess of iodin is then titrated with standard sodium thiosulphate V.S.

$$Hg + I_2 = HgI_2.$$

Mercuric Chlorid may be reduced to mercurous chlorid by means of hydrogen dioxid in the presence of tartaric and hydrochloric acids. Frequent additions of hydrogen dioxid are made and the mixture warmed and filtered. The precipitate is washed and treated as described under assay of mercurous chlorid.

Assay of Mercurous Chlorid or Iodid. The mercurous chlorid or iodid is treated with $\frac{N}{10}$ iodin V.S. and potassium iodid until solution is complete. The reaction is as follows:

$$2HgCl + 6KI + I_2 = 2HgK_2I_4 + 2KCl.$$

The excess of iodin is then titrated with sodium thiosulphate, starch being used as indicator.

The Process. One gm. of the salt, accurately weighed, is heated with 10 mils of distilled water, 50 mils of tenth-normal iodin V.S. and 5 gms. of potassium iodid. The flask is stoppered, and the mixture allowed to stand, with occasional agitation, until complete solution has taken place. The excess of iodin is then titrated as above described.

Each mil of $\frac{N}{10}$ iodin V.S. used corresponds to 0.023606 gm. of HgCl or 0.032752 gm. of HgI.

Reduction Methods Involving the Use of Standard Arsenous Acid Solution (Chlorometry)

As previously described, arsenous oxid when brought in contact with iodin in an alkaline solution, results in an oxidation of the former to arsenic oxid, and a conversion of the iodin to hydriodic acid, as shown in the equation

$$As_2O_3 + 2H_2O + I_4 = As_2O_5 + 4HI.$$

Advantage is taken of this reaction for the estimation, not only of arsenous and antimonous compounds, but also of iodin and the other halogens, chlorin and bromin, as well as of all those bodies which, when heated with hydrochloric acid, evolve chlorin, as for instance the peroxids.

The reaction with chlorin is as follows:

$$Cl_4 + 2H_2O + As_2O_3 = 4HCl + As_2O_5.$$

This reaction is really an oxidation, so far as the formation of arsenic oxid (As_2O_5) is concerned, but there is no accompanying reduction. The conversion of the halogen to an haloid acid is not strictly a reduction in the accepted sense

of the word. Nevertheless, for obvious reasons, we speak of analyses done by means of arsenous acid as reduction methods.

The chief value of this method is found in the estimation of free chlorin, as in chlorin water, and the available chlorin existing in hypochlorites or that evolved from hydrochloric acid by heating with peroxids. Hence the designation "chlorometry."

In carrying out this method free alkali must be present to combine with the haloid acid which is formed. The alkali must be in the form of bicarbonate. Normal carbonates or hydroxids are not suitable (see page 194).

The solutions required are:

Decinormal iodin (see page 188);

Decinormal arsenous acid;

Starch solution (see page 192); or iodized starch test paper.

Preparation of Decinormal $\frac{N}{10}$ Arsenous Acid (As_2O_3 = 197.92; $\frac{N}{10}$ V.S. = 4.948 gms. in 1 liter). 4.948 gms. of the purest sublimed arsenous anhydrid (As_2O_3) are dissolved in a minimum of concentrated sodium hydroxid solution. When complete solution is effected add 100 mils of distilled water and neutralize the excess of alkali with diluted sulphuric acid, using phenolphthalein as indicator. Add to this 20 gms. of pure sodium bicarbonate dissolved in 500 mils of distilled water, and finally dilute to 1000 mils at standard temperature. It is then standardized with decinormal iodin, using starch as indicator. Decinormal arsenous acid solution should correspond, volume for volume, with decinormal iodin solution.

If this solution is made from pure arsenous acid, it will hold its titer for years, but if any sulphur is present there will be an absorption of oxygen from the air and a consequent

oxidation to arsenic oxid. If the presence of sulphur is suspected, the solution should be tested with silver nitrate, when its presence will be indicated by the formation of a reddish precipitate.

Iodized Starch Test Paper. A portion of starch solution is mixed with a few drops of potassium iodid solution and in this are soaked strips of pure white filtering paper. This test paper is used in the damp state; it is then far more sensitive.

Estimation of Free Halogens. The estimation of chlorin, bromin or iodin by the chlorometric method depends, as before stated, upon their power of oxidizing arsenous acid. When a free halogen is brought in contact in alkaline solution with arsenous acid, the latter is oxidized to arsenic acid, while the halogen is transformed into a haloid acid, as per equations

$$\left.\begin{matrix}Cl_4\\Br_4\\I_4\end{matrix}\right\} + 2H_2O + As_2O_3 = As_2O_5 + \left\{\begin{matrix}4HCl\\4HBr.\\4HI\end{matrix}\right.$$

The estimation may be carried out in two ways: 1st, by direct titration with a standard arsenous oxid solution, using iodized starch test paper as indicator; 2d, by residual titration, an excess of the standard arsenous oxid being taken, and then retitrating with standard iodin solution, using starch as indicator. The residual titration method need not be employed for free iodin, as this can be titrated direct with the arsenous oxid solution, using starch as indicator. Furthermore, iodin need not be brought into solution to be titrated by this method.

The estimation of free halogens by the direct chlorometric method is as follows:

An accurately weighed quantity of substance made alkaline by the addition of sodium bicarbonate is titrated with decinormal arsenous acid solution, and from time to time

during the titration a drop of the solution is removed on the end of a pointed glass rod and brought in contact with a piece of iodized starch test paper. So long as free chlorin or bromin is present the liquid will cause a blue stain on the test paper, but when the halogen is all taken up no blue color is produced.

If the exact point is overstepped the residual method must be used. A little additional excess of the arsenous acid solution may be added, together with a few drops of starch solution, and the excess then titrated by means of decinormal iodin solution until the blue color is produced. The volume of decinormal iodin solution so used, deducted from the total volume of arsenous acid solution taken, gives the exact quantity which was oxidized by the halogen, and from this the percentage of chlorin or bromin may be calculated.

Example 1. Estimation of Chlorin in Chlorin Water. Twenty mils of chlorin water (sp.gr. 1.0) titrated by the direct method required 22 mils of decinormal arsenous acid solution before the iodized starch test paper indicated the completion of the reaction.

By referring to the equation we see that each mil of the arsenous acid solution represents 0.003546 gm. of chlorin. Therefore, if 22 mils were used, the 20 mils of chlorin water must have contained 22×0.003546 gm. of chlorin, which is 0.078012.

The 20 mils of chlorin water (sp.gr. 1.0) weigh 20 gms. Hence

$$\frac{0.078012 \times 100}{20} = 39.0+ \text{ per cent.}$$

Example 2. The 20 mils of chlorin water weighing 20 gms. were treated with 26 mils of the arsenous acid solution, starch solution was then added, and the excess of arsenous acid solution titrated by means of decinormal iodin. Four

mils of the latter were required, then 4 from 26 mils leaves 22 mils, the quantity of the $\frac{N}{10}$ arsenous acid solution which reacted with the chlorin. The calculation is the same as in Example 1.

The reaction is as follows:

$$Cl_4 + 2H_2O + As_2O_3 = 4HCl + As_2O_5.$$

$4)141.84$ $\quad$ $4)197.92$

$10)35.46$ $\quad$ $10)49.48$

3.546 gms. = 4.948 gms. = 1000 mils $\frac{N}{10}$ V.S.

0.003546 gms. = 1 mil $\frac{N}{10}$ V.S.

Estimation of Available Chlorin in Bleaching Powder. Three and one-half gms. of the bleaching powder (chlorinated lime) are triturated thoroughly with 50 mils of water, and the mixture transferred to a graduated vessel, together with the rinsings, and made up to 1000 mils with water. This is thoroughly shaken. 100 mils of it (representing 0.35 gm. of the sample) is removed by means of a pipette and titrated with decinormal arsenous acid solution, as described in the foregoing assay, using either the iodized starch test paper as indicator or retitrating the excess of $\frac{N}{10}$ arsenous acid solution added by means of $\frac{N}{10}$ iodin solution.

Each mil of $\frac{N}{10}$ As_2O_3 V.S. represents 0.003546 gm. of available chlorin.

$$Ca(OCl)Cl + As_2O_3 = As_2O_5 + 2CaCl_2.$$

$4)141.84$ $\quad$ $4)197.92$

$10)35.46$ $\quad$ $10)49.48$

3.546 gms. = 4.948 gms. or 1000 mils $\frac{N}{10}$ V.S.

As seen by referring to the above equation this process determines the value of the chlorinated lime by measuring

the amount of arsenous acid which the oxygen present in the active constituent ($Ca(OCl)Cl$) is capable of oxidizing. In the formula of this compound there are two atoms of chlorin and one atom of oxygen. Therefore the quantity of bleaching powder which yields 35.46 parts of available chlorin will also supply 8 parts of oxygen; this may therefore be taken as the measure of the chlorin. The same method may be employed for the assay of all other solutions containing available chlorin.

Assay of Manganese Dioxid (Chlorometric). The chlorometric assay of manganese dioxid, as well as that of all other bodies which liberate chlorin when heated with hydrochloric acid, may be made in similar manner to that described for the iodometric assays of these substances, the same apparatus, etc., being used.

The liberated chlorin is, however, titrated with $\frac{N}{10}$ arsenous acid solution.

The chlorin may be distilled into a solution of sodium carbonate, and this solution is then titrated with $\frac{N}{10}$ arsenous acid or the chlorin may be distilled directly into a measured volume of $\frac{N}{10}$ arsenous acid solution and the latter then titrated with $\frac{N}{10}$ iodin solution, using starch as indicator, the difference between the volume of iodin solution used and that of the arsenous acid solution taken is the measure of the latter which reacted with the chlorin.

It is a good plan in each case to divide the solution into two or three equal parts and to titrate each separately.

Reduction Methods Involving the Use of Stannous Chlorid

Stannous chlorid ($SnCl_2$) is a very powerful reducing agent. Its action in this respect depends npon its affinity for chlorin which it readily abstracts from most other chlorids. In its action upon mercuric chlorid a portion of the latter is always reduced to the metallic state.

This reducing action of stannous chlorid is utilized in certain volumetric processes, especially in the estimation of iron. In this case it possesses an advantage over permanganate, in that the iron must be in the ferric state, in which condition it is most usually found, while if permanganate is used, a preliminary reduction to the ferrous state is necessary before titrating. The great disadvantage, however, is in the fact that even short contact with air will quickly oxidize it, and thus spoil its titer. In consequence of this it must be frequently tested, and can be used only in the form of empirical solutions.

It is particularly useful in the titration of ferric salts, which salts can be accurately estimated by direct titration with it, the end-point being recognized by the disappearance of the yellow color of the ferric solution. These salts may also be estimated residually by adding an excess of stannous chlorid solution of known strength and retitrating the excess by means of standard iodin, using starch as indicator.

The reactions are:

$$Fe_2Cl_6 + SnCl_2 = 2FeCl_2 + SnCl_4$$

and

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI.$$

The Estimation of Iron by Means of Stannous Chlorid Solutions may be accurately affected by the following procedure, as suggested by Fresenius. The solutions necessary are:

(*a*) A solution of ferric chlorid containing 10 gms. of pure iron in a liter.

This is made by dissolving 10.04 gms. of thin annealed binding wire (which contains 99.6 per cent of pure iron) in a sufficient quantity of pure hydrochloric acid. A small quantity of potassium chlorate is then added to effect complete oxidation of the iron, and the excess of chlorin expelled by boiling. This solution is then cooled and diluted to 1 liter.

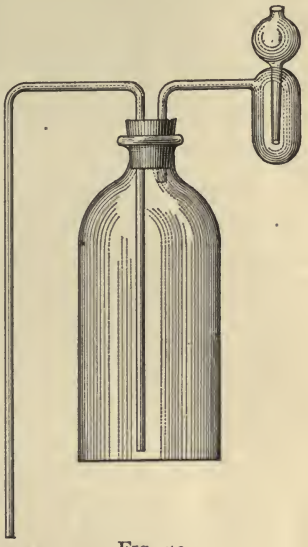


Fig. 53.

(*b*) A solution of stannous chlorid made by dissolving about 10 gms. of pure tin in 200 mils of strong, pure hydrochloric acid. This may be done by heating the tin in small pieces with the acid in a flask, and introducing a few pieces of platinum foil to excite galvanic action. The solution so obtained is diluted to about one liter with distilled water and should be preserved in a bottle, such as shown in Fig. 53, to which air can only gain access through a strongly alkaline solution of pyrogallic acid. When so kept the strength of the solution can be preserved for several weeks.

(*c*) A solution of iodin in potassium iodid. This may be approximately or exactly decinormal.

The procedure is as follows:

1st. The relation between the tin solution and the iodin solution is found.

2d. The relation between the tin solution and the iron solution is determined.

3d. The assay.

The relation between the tin solution and the iodin solution is found as follows:

Two mils of the tin solution are put into a beaker, a little starch solution added, and the iodin solution then delivered in from a burette until the blue color occurs. If 4 mils are used, then each 2 mils of iodin solution represents 1 mil of tin solution.

The relation between the tin solution and the iron solution is found as follows:

Fifty mils of the iron solution (representing 0.5 gm. of iron, are put into a small flask together with a little hydrochloric acid and heated to gentle boiling. The tin solution is then delivered from a burette until the yellow color of the iron solution is nearly discharged. It is then added continuously, drop by drop, until the color is entirely gone. Assuming that 35 mils were required, then each 35 mils of tin solution are equivalent to 0.5 gm. of pure iron. If the end-point is not clearly recognized and an excess of the tin solution was added, the solution should be quickly cooled, a few drops of starch solution added, and the excess estimated by titrating with the iodin solution, each mil of which represents 0.5 mil of the tin solution. The excess so found, deducted from the total quantity of tin solution added, gives the quantity of the latter, which corresponds to 0.5 gm. of iron.

Having determined these data, the analyst can readily estimate any unknown quantity of iron in solution in the ferric state.

If the iron is partly or wholly in the ferrous state it may be oxidized by adding some potassium chlorate and boiling to expel excess of chlorin.

The Assay. A solution of iron taken for analysis, required 24 mils of the tin solution. The quantity of iron present is calculated by proportion as follows:

$$35 \text{ mils} : 0.5 \text{ gm.} :: 24 \text{ mil} : x; \qquad x = 0.34 \text{ gm.}$$

To secure accurate results the iron solution assayed must be fairly concentrated, because then the end-reaction is more readily seen, and also because the greater the dilution the larger the amount of tin solution will be required. It is good policy to use very little excess of the tin solution, so that only a very small quantity of iodin solution is required.

Estimation of Mercuric Salts (Laborde). This depends upon the fact that stannous chlorid solution added to a solution of a mercuric salt reduces the latter first to mercurous chlorid (calomel) and finally the calomel to metallic mercury. The reduction to calomel results in the formation of a white precipitate, and when the mercuric salt is completely reduced the stannous chlorid acts upon and reduces the calomel to metallic mercury, which results in the production of a characteristic brownish color.

The reactions are as follows:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl;$$

$$SnCl_2 + 2HgCl = SnCl_4 + Hg_2.$$

According to Laborde the tin solution is made by dissolving 8 gms. of pure tinfoil by means of heat in 100 mils of pure hydrochloric acid, and diluting to 2 liters.

This tin solution is checked against a solution of mercuric chlorid containing 10 gms. per liter. To counteract the hindering effect of the hydrochloric acid the solution under analysis, containing 0.1 gm. of mercuric chlorid, is mixed with 5 mils of a solution containing 100 gms. of ammonium acetate and 100 mils of acetic acid to the liter. The acetic acid promotes the disappearance of the brown color which occurs at the point where the tin solution is in excess, but before reduction is complete. The titration with the tin solution is continued until a permanent brown color occurs.

If the brown color is too dark from overstepping of the end-point, the addition of 1 mil of the mercuric chlorid solution will render the solution white again, and the titration can then be carried further.

This method, which is convenient, rapid, and very accurate, can be employed in many cases. If the mercuric solution contains any free mineral acids, the latter must be neutralized with ammonia (in the presence of ammonium acetate, to prevent formation of ammoniated mercury).

The presence of alkali and alkali earth salts or most salts of other metals (except iron, gold, and platinum) do not in the least interfere with the accuracy of the results. The same is true of organic acids, either free or in combination with alkali.

PART II

CHAPTER XI

ESTIMATION OF ALKALOIDS

In making alkaloidal assays of drugs it has long been the custom to evaporate the final ethereal or chloroformic extract, and to weigh the residue as alkaloid. This residue seldom, if ever, consists of the pure alkaloid, and the impurities—i.e., non-alkaloidal matter—is variable in amount and difficult to entirely remove, consequently gravimetric results are in many cases very wide of the truth, and hence unreliable.

The volumetric methods are in most cases much more satisfactory.

While the results of the titration of the *total alkaloids* of drugs cannot be called absolutely accurate, nevertheless experience has shown that they are nearer the truth than those obtained by the gravimetric method.

In estimating an alkaloid by titration it is essential to know the formula and molecular weight of the alkaloid, as well as the equivalent of acid with which it will combine.

The quantity of alkaloid present is easily calculated when we know that a molecular weight of a monobasic acid or half a molecular weight of a dibasic acid will combine with and neutralize a molecular weight of an alkaloid, provided the alkaloid is a monacid base. If the alkaloid is a diacid base, one molecular weight will combine with two molecules of a monobasic acid or one molecular weight of a dibasic acid.

Sparteine and emetine (?) are diacid alkaloids; most of the others are monacid bases.

Examples. Monacid alkaloids:

$$\underset{\text{Quinine}}{C_{20}H_{24}N_2O_2} + HCl = C_{20}H_{24}N_2O_2.HCl;$$

$$\underset{\text{Morphine}}{(C_{17}H_{19}NO_3)_2} + H_2SO_4 = (C_{17}H_{19}NO_3)_2.H_2SO_4;$$

$$\underset{\text{Strychnine}}{(C_{21}H_{22}N_2O_2)_2} + H_2SO_4 = (C_{21}H_{22}N_2O_2)_2.H_2SO_4;$$

Diacid alkaloids:

$$\underset{\text{Sparteine}}{C_{15}H_{26}N_2} + 2HCl = C_{15}H_{26}N_2(HCl)_2;$$

$$\underset{\text{Emetine (Kunz)}}{C_{30}H_{40}N_2O_5} + H_2SO_4 = C_{30}H_{40}N_2O_5.H_2SO_4.$$

The quantity of alkaloid present in the substance is easily calculated, as illustrated by this equation:

$$\underset{\text{Quinine}}{C_{20}H_{24}N_2O_2} + HCl = C_{20}H_{24}N_2O_2.HCl.$$

324.2 gms. 36.46 gms. = 1000 mils $\frac{N}{1}$ V.S.;

32.42 " 3.646 " = 1000 mils $\frac{N}{10}$ V.S.

Thus 1 mil of $\frac{N}{10}$ V.S. = 0.03242 gm. of quinine.

$$\underset{\text{Sparteine}}{C_{15}H_{26}N_2} + 2HCl = C_{15}H_{26}N_2(HCl)_2.$$

$\underset{117.1 \text{ gms.}}{2)234.2}$ $\underset{36.46 \text{ gms.} = 1000 \text{ mils } \frac{N}{1} \text{ V.S.};}{2)72.92}$

11.71 " 3.646 " = 1000 mils $\frac{N}{10}$ V.S.

One mil of $\frac{N}{10}$ V.S. hence = 0.01171 gm. of sparteine.

Thus 1000 mils of $\frac{N}{10}$ hydrochloric acid will combine with

$\frac{1}{10}$ of the molecular weight in grams of a monacid alkaloid, or $\frac{1}{2}\frac{1}{0}$ of the molecular weight of a diacid alkaloid.

In the case of drugs where two or more alkaloids are present, accurate results can only be obtained by determining how much of each alkaloid is present by a separate assay. But often it is assumed that the alkaloids are present in equal quantities, and the mean of their molecular weights is taken as the basis for the calculation.

It must be borne in mind, however, that in titrating alkaloids the *greatest care* must be exercised and all precautions closely observed in order to attain any degree of accuracy. The volumetric solutions must be prepared with the greatest care and must be absolutely accurate. The eye must be trained (as it can only be through practice), to distinguish the end-colors of the indicators employed, a matter of some difficulty. Furthermore, all measuring instruments used must be accurate, or they should be carefully calibrated in order to find the necessary factor for correction.

The Volumetric Solutions usually employed in titrating alkaloids are $\frac{N}{10}$, $\frac{N}{20}$, $\frac{N}{25}$, $\frac{N}{50}$, and $\frac{N}{100}$. The weaker solutions give more accurate results, as will be understood if we remember that a $\frac{N}{1}$ is 10×stronger than a $\frac{N}{10}$ and 100×stronger than $\frac{N}{100}$ V.S. Then if $\frac{N}{1}$ solution be used, one drop may overstep the neutral point, while if the same solution were treated with $\frac{N}{10}$ solution 5 drops would be required to neutralize, which is equivalent to using one half a drop of $\frac{N}{1}$ solution. A $\frac{N}{100}$ solution will of course be capable of even more delicate

work. In the case just mentioned 45 drops of the $\frac{N}{100}$ may exactly neutralize the solution, hence less than half a drop of $\frac{N}{1}$ and between 4 and 5 drops of $\frac{N}{10}$ are represented. Therefore in all delicate alkaloidal titrations weak standard solutions should be used—in fact, in all titrations where great accuracy is required.

If the alkaloid be from a recent extraction and is in the form of a free alkaloid, it is dissolved in a measured volume of $\frac{N}{10}$ acid solution and the excess of acid solution then determined by residual titration with $\frac{N}{100}$ alkali solution.

In this the $\frac{N}{10}$ sulphuric acid solution is preferred, except in the case of quinine or cinchonine, in which $\frac{N}{10}$ hydrochloric acid gives better results.

The process in detail is as follows: Place 2 gms. of the alkaloid into a beaker, add 75 mils of $\frac{N}{10}$ sulphuric acid solution, and warm on a water-bath until the alkaloid is completely dissolved. The solution is then allowed to cool and diluted to 100 mils.

Ten mils of the solution (containing 0.2 gm. of the alkaloid and 7.5 mils of $\frac{N}{10}$ sulphuric acid solution) are removed by means of a pipette and retitrated with $\frac{N}{100}$ potassium hydroxid solution. One-tenth of the quantity of the $\frac{N}{100}$ alkali used is deducted from the 7.5 mils of the $\frac{N}{10}$ acid solution, and the

remainder is the quantity of the latter which combined with and hence represents the alkaloid present. This, if multiplied by the factor, gives the weight of the alkaloid.

Either hæmatoxylin solution or Brazil-wood T.S. may be employed as the indicator.

If the alkaloid is soluble in alcohol, as are quinine and codeine, it may be treated as follows:

Place 2 gms. of the alkaloid in a graduated cylinder, dissolve in alcohol, and dilute the solution up to 100 mils with alcohol. Remove 10 mils of this solution (containing 0.2 gm. of the alkaloid) and place in a beaker, add the indicator and run in the decinormal acid solution to slight excess. Rotate the beaker several times, let stand for a few minutes, wash down the sides of the beaker with distilled water, using about 40 mils, and retitrate the excess of acid with $\frac{N}{100}$ potassium hydroxid solution, until end-color is given by the indicator. Deduct one-tenth of the quantity of the $\frac{N}{100}$ solution used from the quantity of $\frac{N}{10}$ acid solution added, and the remainder is the quantity of the latter, which combined with and hence represents the alkaloid present.

The indicators best suited for most alkaloids are *Hæmatoxylin*, *Brazil-wood*, *Cochineal*, *Iodeosin* and *Litmus*.

The color changes produced by the principal indicators used in alkaloidal titrations are as follows:

	Acid.	Alkali.
Hæmatoxylin	Yellow	Blue
Brazil-wood	"	Purplish-red
Cochineal	Yellowish-red	Purplish
Litmus	Red	Blue
Iodeosin	Yellow	Rose-red
Lacmoid	Red	Blue
Fluorescein	Green fluorescence	No fluoresc., yellowish
Congo red	Blue	Red
Methyl-orange	Red	Straw-yellow
Phenolphthalein	Colorless	Red

TABLE SHOWING THE FACTOR FOR VARIOUS ALKALOIDS WHEN TITRATING WITH $\frac{N}{10}$ ACID OR ALKALI

Name.	Formula.	Molecular Weight.	Factor.
Aconitine	$C_{34}H_{47}NO_{11}$	645.48	0.064548
Atropine	$C_{17}H_{23}NO_3$	289.24	0.028924
Brucine	$C_{23}H_{26}N_2O_4$	394.28	0.039428
Cephaeline	$C_{14}H_{19}NO_2$	233.20	0.023320
Cinchona alkaloids (combined)	.....	.....	0.03069
Cinchonine	$C_{19}H_{22}N_2O$	294.24	0.029424
Cinchonidine	$C_{19}H_{22}N_2O$	294.24	0.029424
Cocaine	$C_{17}H_{21}NO_4$	303.22	0.030322
Codeine	$C_{18}H_{21}NO_3$	299.22	0.029922
Coniine	$C_8H_{17}N$	127.18	0.012718
Emetine	$C_{30}H_{44}N_2O_4$ (Glenard)	496.32	0.024818
	$C_{30}H_{40}N_2O_5$ (Kunz)	508.34	0.025417
	$C_{15}H_{21}NO_2$ (U. S. P.)	247.22	0.024722
Hydrastine	$C_{21}H_{21}NO_6$	383.22	0.038322
Hyoscine	$C_{17}H_{21}NO_4$	303.18	0.030318
Hyoscyamine	$C_{17}H_{23}NO_3$	289.24	0.028924
Ipecac alkaloids (combined)	.....	.....	0.024021
Morphine	$C_{17}H_{19}NO_3$	285.20	0.02852
Nicotine	C_5H_7N	81.06	0.008106
Physostigmine	$C_{15}H_{22}N_3O_2$	275.24	1.027524
Pilocarpine	$C_{11}H_{16}N_2O_2$	208.18	0.020818
Quinine	$C_{20}H_{24}N_2O_2$	324.26	0.032426
Sparteine	$C_{15}H_{26}N_2$	234.28	0.011714
Strychnine	$C_{21}H_{22}N_2O_2$	334.24	0.033424

GORDIN'S MODIFIED ALKALIMETRIC METHOD, USING PHENOLPHTHALEIN AS INDICATOR

The alkaloidal residue obtained by any of the extraction methods in use is dissolved in a measured excess of $\frac{N}{20}$ hydrochloric acid solution. Wagner's or Mayer's reagent is then added, a little at a time, with frequent shaking, until the alkaloids are completely precipitated. The mixture is then diluted with water to 100 mils and shaken until the double salt of the alkaloid and reagent completely separate. When allowed to stand a few minutes the supernatant liquid should be clear, and if Wagner's reagent has been used, this will be of a dark-red color. The liquid is now filtered, and 50 mils of the filtrate (representing one-half of the alkaloid) is treated with a 10 per cent solution of sodium thiosulphate added, drop by drop, until the color of the free iodin disappears. This discolorization is not needed if Mayer's reagent has been used. A few drops of the indicator phenolphthalein are now introduced, and the excess of acid estimated by retitration with $\frac{N}{20}$ potassium hydroxid solution. This, deducted from one-half of the volume of the standard acid solution employed, indicates the number of mils of $\frac{N}{20}$ hydrochloric acid solution, which combined with the alkaloid in 50 mils of the solution. This number, multiplied by two and then by the factor for the alkaloid present, gives the total quantity of alkaloid.

Example. An alkaloidal residue consisting of morphine was dissolved in 30 mils of $\frac{N}{20}$ HCl V.S. Then Wagner's reagent was added in excess as described, and the mixture made up

to 100 mils with water. Fifty mils of this were filtered off, decolorized as directed, and titrated with $\frac{N}{20}$ KOH V.S. Ten mils were required, which corresponds to 20 mils for the entire quantity. Then 20 mils deducted from the 30 mils of $\frac{N}{20}$ HCl V.S. added, leaves 10 mils, the quantity required to neutralize the morphine. The $\frac{N}{20}$ factor for morphine (0.0137 gm., Gordin), multiplied by 10=0.137 gm., the quantity of alkaloid in the residue examined.

The $\frac{N}{10}$ factor for morphine here given is somewhat lower than the theoretical equivalent. It was ascertained by experment with a sample of the anhydrous alkaloid.

The following factors (by Gordin) were obtained by comparing their molecular weights with that of morphine, which factor was determined by experiment:

Morphine	0.0137 gm.	=	1 mil $\frac{N}{20}$	HCl V.S.
Hydrastine	0.0184 "	=		
Strychnine	0.0160 "	=		"
Caffeine, cryst.	0.0102 "	=		"
Cocaine	0.0146 "	=		"
Atropine	0.0139 "	=		"

CHAPTER XII

VOLUMETRIC ASSAYING OF VEGETABLE DRUGS AND THEIR PREPARATIONS

EXTRACTION OF THE ALKALOIDS

Selection of the Sample. Care must be taken to secure a fairly representative sample.

If the drug is in small pieces or consists of seeds or leaves, mix it well, take a portion, pulverize it, and of the powder take a sufficient quantity for the assay. If the drug be in large lumps, which vary in quality, select a few representative lumps and cut from each a fairly representative section; pulverize these, mix well, and weigh off a sufficient quantity for the assay.

If drying is necessary, the loss of weight in drying must be made note of.

The Exhaustion of the Drug is usually effected by maceration in a suitable menstruum, although percolation, boiling, and hot repercolation must be employed in some cases.

The Choice of Solvent depends upon the nature of the drug. Water dissolves, besides the alkaloids, so much inert matter that the subsequent steps in the assay are liable to be interfered with. Alcohol dissolves too much of the resinous matter, and besides does not penetrate the drug very well. Acidulated water has been much used, but chloroform and ether, separately and in various combinations, are now most generally employed for exhausting drugs in conjunction with

alcohol and ammonia. Petroleum benzin has of late been recommended.

Prollius' fluid, or some modification of it, is very satisfactory.

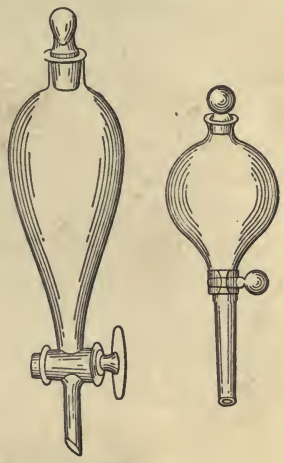
Prollius' Fluid consists of ether 325 mils, alcohol 25 mils, and concentrated ammonia-water 10 mils.

Modified Prollius' Fluid consists of ether 250 mils, chloroform 80 to 100 mils, alcohol 25 mils, concentrated ammonia-water 10 mils.

The Separation of the Alkaloids and the Use of Immiscible Solvents. *"The Shaking-Out" Process.* Most alkaloids are insoluble in water but are readily soluble in certain "volatile solvents" such as alcohol, ether, chloroform, amyl alcohol, benzene, petroleum benzin, acetic ether, etc., but not in carbon tetrachlorid. Those alkaloidal solvents which do not mix readily with water are known as "the immiscible solvents." Salts of alkaloids on the other hand are as a rule soluble in water, but practically insoluble in the immiscible solvents. This property of the alkaloids makes it possible to separate them from their natural sources.

The alkaloid in solution in an immiscible solvent may be separated by "shaking out" with a dilute acid, the alkaloid is thereby converted into an alkaloidal salt which readily dissolves in the aqueous acid solution. Conversely, an aqueous solution of an alkaloidal salt when treated with an alkali to set free the alkaloid and shaken with an immiscible solvent gives up its alkaloid in a pure state to the latter. The process of assay by this "shaking-out" process is carried out by treating the liquid extracts (after having been freed from alcohol) with an immiscible solvent and a slight excess of an alkali. The alkaloid is thus dissolved in the immiscible solvent, which is then separated from the aqueous liquid, and transferred to another vessel in which it is shaken with an

excess of acid largely diluted with water. The acid combines with the alkaloid and forms an alkaloidal salt, which leaves the immiscible solvent, and enters the aqueous solution. If the alkaloidal solution so obtained is still colored, the shaking out is repeated until a pure alkaloidal solution in the immiscible solvent is obtained. The apparatus used in this shaking-out operation is known as a separator. See Fig. 54.



Squibb's Pattern

FIG. 54.

Separators are conical or pear-shaped; the neck is provided with a well-ground glass stopper and the outlet tube or stem at the bottom with an accurately-fitting glass stopcock. The solvents usually used in alkaloidal drug assaying are alcohol, chloroform, ether and various mixtures of these containing at least 75 per cent of ether. When chloroform is used it will collect at the bottom of the separator, and can be easily drawn off; but if ether, or ether-chloroform mixture is used, it will form the upper layer in the separator, and may be syphoned off, or the lower aqueous layer drawn off, and the ethereal layer then transferred to another separator. Violent shaking of the contents of the separator is to be avoided, gentle shaking or rotating is quite sufficient to bring about the desired transfer of alkaloid. Excessive shaking will cause the formation of an emulsion of the water and solvent, which is often hard to break up.

The final operation should always be the collection of the free alkaloid by means of a portion of the immiscible solvent. This solution is drawn off into a beaker, the solvent evap-

orated over a water-bath, using gentle heat, and the dry residue in the beaker dissolved in a measured quantity of standard acid V.S. The excess of acid V.S. is then titrated with a standard alkali V.S. in the presence of a suitable indicator.

In connection with this, attention is called to the fact that some of the most important methods of isolating alkaloids in drug assays and in toxicological investigations depend upon the solubility of the free alkaloids in ether, chloroform, benzene, etc., and the relative insolubility of alkaloidal salts in the same solvents. There are, however, a number of exceptions to this rule, and special attention is called to the fact that in many cases alkaloids pass from decidedly acid aqueous solutions (in which they certainly occur as alkaloidal salts) into chloroform and ether, in the shaking-out methods. While the amount of alkaloid so dissolved by these solvents is never very great, still the quantity is an appreciable one. This behavior occurs in the case of caffeine, colchicine, and narcotine; and under certain conditions also in the case of strychnine, atropine, veratrine and other bases. This transfer of alkaloid to chloroform occurs more particularly in the case of alkaloids of weak basic character, and when the solution is neutral or only feebly acid, or when the alkaloid is in combination with a comparatively weak acid, as citric, tartaric, etc. Furthermore, some alkaloidal salts, notably those of weak bases, are transferred as such to chloroform, especially the salts of hydrochloric acid, hydrobromic acid, and nitric acid. In the case, however, of the sulphates, phosphates, tartrates, and citrates of strongly basic alkaloids, no transfer occurs, or at most, only minute quantities of the alkaloids pass over. In order to prevent a transfer of alkaloid or alkaloidal salt out of an aqueous solution to an immiscible solvent, the use of sulphuric acid is to be recommended, and in all toxicological

investigations due regard should be paid to the above named conditions. For more details, see the paper by Edward Schaer, Proc. A. Ph. A., 1906, 425.

GENERAL METHODS OF ASSAYING DRUGS

No rule can be formulated as to the method of extraction, or the solvent to be employed, which can be applied to all drugs. Each must be dealt with in accordance with the properties of the contained alkaloids and their state of combination. Several methods, however, are in use which may be applied to a large number of different drugs, and with slight special modifications to many more.

Kebler's Modification of the Keller Method.* Treat 10 gms. of the dry powdered drug in a 250-mil flask with 25 gms. of chloroform and 75 gms. of ether: stopper the flask securely, agitate well for a few minutes and add 10 gms. of ammonia-water and shake frequently during one hour. Then on adding 5 gms. more of the ammonia-water and shaking, the suspended powder agglutinates into a lump, leaving the solution clear after a few minutes' standing. Then proceed by A or B.

A. When the mixture has completely separated, 50 gms. (representing 5 gms. of the drug) are poured off into a beaker and heated on a water-bath until the solvent is evaporated. Ten mils of ether are then added and again evaporated. The varnish-like residue is then dissolved in 15 mils of warm alcohol and water added to slight permanent turbidity, then the indicator is added, followed by an excess of standard acid solution, and the mixture retitrated with standard alkali.

B. When the mixture has completely separated, pour off 50 gms. into a separatory funnel, and add 20 mils of acidulated water, agitate, and when the liquids have separated draw

* J. A. C. S., XVII, 828.

off the aqueous solution into a second separatory funnel. Repeat this operation with two more portions of 15 mils of acidulated water. Now render the contents of the separatory funnel alkaline by adding ammonia-water. This liberates the alkaloids, which are then separated by treatment with a mixture of chloroform, three parts (by volume), and ether, one part, using three successive portions, first 20 mils, then twice 15 mils.

The chloroform-ether solution is heated on a water-bath until the solvent is evaporated, and then the varnish-like residue treated twice with 8 mils of ether and again evaporated.

The residue is then dissolved in 15 mils of alcohol, water added to slight permanent turbidity, and then the indicator. Titrate in usual way with decinormal acid and centinormal alkali.

A serious objection to this method lies in the taking of a so-called aliquot part: First, because of the well-known solubility of ether in water, and conversely of water in ether, as a result of which the volume of the ethereal stratum is materially changed. Furthermore, commercial ether contains variable quantities of alcohol, hence the change in volume will not always be the same.

Another source of error in the aliquot part is found in the volatile nature of the solvents used. In warm weather it is impossible to avoid loss by volatilization, hence the aliquot part taken is too large.

W. A. Puckner * has described a modification of the Keller method which avoids the use of the aliquot part. He uses only one-half of the ethereal solvent for the maceration, and after the usual maceration transfers the drug to a small percolator in which, after the ethereal solution has been well

* Ph. Rev. XVI, 180, and XX, 457.

drained off, the marc is percolated with the same menstruum to complete exhaustion. The quantity of ethereal solvent required is not materially greater than in the Keller method, while the quantity of alkaloid obtained for weighing or titrating is larger because it represents the whole of the sample taken for the assay. In the case of drugs containing a very small proportion of alkaloid this is an important advantage.

The objection to this plan is that the transfer of the mass from the flask in which the maceration has been conducted to a suitable percolator, which should not be more than 3 cm. in diameter, requires very dextrous manipulation, or it will be attended with loss of alkaloid.

Assay of Galenical Preparations.

J. U. Lloyd's Method. One gm. of a solid extract which has been dissolved in 5 to 8 mils of an alcoholic menstruum or a corresponding volume of the tincture evaporated to this bulk, or 5 mils of the fluid extract in a flat-bottomed porcelain mortar, are mixed with 2 mils of a solution of perchloride of iron. To this is added sodium bicarbonate with constant trituration until a stiff magma * results. Extract this magma by repeated trituration with chloroform, using first 20 mils and then three portions of 10 mils each, decanting them severally by means of a guiding-rod, being careful that no suspended portions of the magma are drawn off. In order to make sure that all of the alkaloid has been extracted, add 5 mils more of chloroform, draw it off, evaporate on a watch-glass, dissolve

* The ferric hydroxid which is produced in the above process serves to attract most of the tannates, gums, vegetable acids, and coloring matters, while the excess of sodium bicarbonate liberates the alkaloids, which are then dissolved by the chloroform. If the fluid extract is strongly alcoholic the chloroform will not separate easily, in which case the addition of a few mils of water containing a very little glucose will cause a sharp separation.

residue in dilute sulphuric acid, and test for alkaloids by Wagner's or Mayer's reagent.

The mixed chloroformic extracts are collected and may be estimated volumetrically as follows:

METHOD A. To be used if the chloroformic extract is not colored.

The chloroformic solution is evaporated to dryness in a flask placed on a water-bath. To this residue is added an accurately measured excess of $\frac{N}{25}$ sulphuric V.S. and the solution diluted with a little water, the indicator added and the excess of standard acid solution estimated by titrating with $\frac{N}{50}$ potassium hydroxid V.S. The number of mils of the $\frac{N}{50}$ alkali V.S. used, divided by 2 and subtracted from the volume of $\frac{N}{25}$ acid V.S. originally added, will give the number of mils of the latter required for the alkaloid. This number, multiplied by the proper factor, will give the total alkaloid present in the fluid extract.

Example. The chloroformic residue obtained from 5 mils of a fluid extract of hyoscyamus was dissolved in 12 mils of $\frac{N}{25}$ acid V.S., the solution titrated with $\frac{N}{50}$ alkali V.S. 20.6 mils of the latter were used.

20.6 mils of $\frac{N}{50}$ V.S. is the equivalent of 10.3 mils of $\frac{N}{25}$ V.S. 10.3 mils subtracted from 12 mils, the amount of $\frac{N}{25}$ acid originally added, leaves 1.7 mils, the quantity of $\frac{N}{25}$ acid V.S. which was required for the alkaloid. This, multiplied by the

$\frac{N}{25}$ factor for total alkaloids of hyoscyamus, 0.01157 gm., gives the quantity of alkaloids present in the 5 mils, which quantity multiplied by 20 gives the per cent:

$$1.7 \times 0.01157 = 0.019669 \text{ gm.} \times 20 = 0.39338 \text{ per cent.}$$

METHOD B. This method may be employed if the chloroformic extract is highly colored, the indicator fluorescein being used.

The residue from the evaporation of chloroform is dissolved in 10 mils of acid-free alcohol; then water is added to slight turbidity, followed by a measured excess of $\frac{N}{25}$ acid V.S.; then the titration is completed with $\frac{N}{50}$ alkali V.S. The first appearance of fluorescence marks the completion of the reaction. This is best observed by holding the flask over a dark surface and viewing by reflected light.

METHOD C. This is to be used in the case of highly colored extracts. It consists in removing the alkaloid in a pure state by shaking out in a separating funnel with immiscible solvents. The chloroformic extract is shaken out with several portions of acidulated water; this removes the alkaloid, leaving resins, fats, coloring matters, etc., in the chloroform. The acid alkaloidal solution is then treated with ether in a second separator, ammonia added to alkaline reaction, and the alkaloid thus liberated by ammonia dissolves in the ether, from which it is obtained by evaporation and estimated acidimetrically.

ANOTHER METHOD. Add ammonia and shake out directly with an immiscible solvent. Wash the alkaloid out of this with acidulated water and again shake out with a suitable immiscible solvent.

J. Katz's Method (*Arch. d. Pharm.*, 1898, 1; *Am. Dr.*, 1898, 281). This method has the advantage of all other methods

in that it enables one to rapidly and accurately estimate the alkaloids in a preparation without the necessity of applying heat for any purpose whatever during the process. The assay may be made in from one to three hours. Twenty-five mils of the tincture of an alcoholic strength of about 45 per cent are placed in a separatory funnel, 1 mil of a 33 per cent solution of soda added, and the mixture shaken for five minutes with 50 mils of ether, and set aside until the liquids have completely separated into two layers. The lower dark-colored aqueous layer is drawn off into a beaker. The ethereal layer which, besides the alkaloid, has taken up most of the alcohol and some coloring matter, is shaken up with 3 mils of water which, after separating, is drawn off and added to the first aqueous liquid. The ethereal liquid is then poured into a suitable flask, while the combined aqueous liquid is further treated with two portions of ether (25 mils each) the ether to contain about 10 per cent of alcohol. These ethereal extractions are washed each with 1.5 mils of water; the first extraction after washing may be added to the original ethereal solution, while the second is reserved and later on employed for washing the flask. The ethereal solution, which contains still some traces of aqueous fluid containing alkali, is dehydrated by treatment with 2 or 3 gms. of exsiccated calcium sulphate, and finally filtered into a glass-stoppered flask containing 50 mils of water.

Titration by means of $\frac{N}{100}$ acid V.S. is employed, using alcholic solution of iodeosin (1–250) as indicator.

The Method as above described is obviously applicable only to such alkaloids as are readily soluble in ether. If an estimation of alkaloids insoluble or only slightly soluble in ether, but soluble in chloroform, is to be made, the method is modified as follows:

Twenty-five mils of the tincture of 45 per cent alcoholic strength are vigorously shaken for five minutes with 30 mils of a mixture of 1 part of chloroform and 2 parts of ether. The solution so obtained is washed with 3 mils of a 30 per cent solution of sodium chlorid. This operation is repeated twice, using each time 15 mils of the ether-chloroform mixture and washing with 1.5 mils of sodium chlorid solution.

If the Separation of the aqueous and ethereal liquids is not distinct an additional 2 or 3 gms. of sodium chlorid may be used. This prevents the emulsification, which, if pure water were employed, would occur.

If the Tincture to be assayed contains more than 45 per cent of alcohol it is necessary to add water to reduce it to 40 or 50 per cent.

Tinctures containing Chlorophyll or fat or fatty acids must first be deprived of these constituents, as these substances, possessing acid properties inferior to that of iodeosin, will act the part of an alkali toward it and thus be recorded as alkaloid.

To remove the Chlorophyll and fatty acids, acidulate a mixture of equal parts of the tincture and water with a few drops of sulphuric acid, shake with talcum during several hours, and, after subsidence of the latter, filter. Of this filtrate 25 gms. (not mils, on account of the admixture of alcohol and water causing change of volume) are taken and the alkaloid estimated in the manner already described, after first removing, if necessary, the last traces of fat by a single shaking of the acid solution with petroleum ether.

For the Assay of extracts 1 to 1.5 gms. are dissolved in from 40 to 50 mils of 45 per cent alcohol to make a solution containing less than 3 per cent extractive. For the assay of fluid extracts 10 mils are taken.

For details of special assays, see the author's Manual of Volumetric Analysis.

The Influence of the Presence of Certain Volatile Solvents upon the accuracy of alkaloidal titrations must be borne in mind. Alcohol in may instances influences the color changes of the indicators to the extent of rendering them indistinct or entirely unreliable; while ether or chloroform materially diminishes the sensitiveness of many of our most valued indicators, among them phenolphthalein, rosalic acid, congo-red, and luteol. On the other hand, fluorescein and gallein may be mentioned as being more sensitive in the presence of alcohol or even of ether. It is advisable, therefore, in most cases, to perform the titration without the presence of the above-named solvents.

Indicators Vary in their Degree of Sensitivenness to the same Alkaloid, hence the choice of an indicator in a particular case is a matter of importance. The following table, based upon that of Kippenberger, will serve as an aid in the selection. The smallest quantity which will procure a distinct tint should be taken.

Atropine.	*Lacmoid, Fluorescein,* Iodeosin, Hæmatoxylin.
Brucine.	*Cochineal,* Iodeosin, Hæmatoxylin.
Cocaine.	*Lacmoid,* Fluorescein, Cochineal, Hæmatoxylin.
Coniine.	*Cochineal, Lacmoid,* Iodeosin, Hæmatoxylin.
Codeine.	*Iodeosin, Lacmoid,* Hæmatoxylin.
Emetine.	*Iodeosin,* Cochineal.
Morphine.	*Hæmatoxylin, Cochineal,* Lacmoid.
Quinine.	*Hæmatoxylin, Azolitmin,* Fluorescein.
Strychnine.	*Azolitmin,* Iodeosin, Hæmatoxylin.
Sparteine.	*Hæmatoxylin,* Azolitmin.

CHAPTER XIII

ESTIMATIONS INVOLVING USE OF DECINORMAL BROMIN V.S.

Preparation of Decinormal Bromin V.S. (Koppeschaar's Solution), Br = 79.92; 7.992 gm. in 1 liter.

KBr = 119.02	NaBr = 102.92
$KBrO_3$ = 167.02	$NaBrO_3$ = 150.92

This solution does not contain free bromin, but it contains two salts, a bromid and a bromate, which, when treated with hydrochloric acid, liberate a definite quantity of bromin.

It is made as follows: Dissolve 3 gms. of sodium bromate and 50 gms. of sodium bromid (or 3.2 gms. of potassium bromate and 50 gms. of potassium bromid) in sufficient water to make 900 mils.

Transfer 20 mils of this solution by means of a pipette into a bottle having a capacity of about 250 mils, provided with a glass stopper; add 75 mils of water, then 5 mils of pure hydrochloric acid, and immediately insert the stopper.

Shake the bottle a few times, then remove the stopper just sufficiently to quickly introduce 5 mils of potassium iodid solution (1–5), taking care that no bromin vapor escape, and immediately stopper the bottle.

Agitate the bottle thoroughly, remove the stopper and rinse it and the neck of the bottle with a little water so that the washings flow into the bottle, then add from a burette decinormal sodium thiosulphate until the color of the free iodin is nearly all discharged, then add a few drops of starch

solution, and continue the titration with $\frac{N}{10}$ thiosulphate V.S. until the blue color disappears.

Note the number of mils of the $\frac{N}{10}$ sodium thiosulphate thus used, and dilute the bromin solution so that equal volumes of it and the $\frac{N}{10}$ sodium thiosulphate will exactly correspond to each other under the above-mentioned conditions.

Example. Assuming that the 20 mils of bromin solution required 25.2 mils of the $\frac{N}{10}$ thiosulphate to completely absorb the iodin, the bromin solution must be diluted in the proportion of 20 to 25.2; that is, each 20 mils must be diluted to make 25.2 mils.

Thus if 850 mils are left, they must be diluted to make 1071 mils, and the solution is decinormal.

A new trial should always be made after diluting, and the bromin solution should correspond, volume for volume, with the decinormal sodium thiosulphate.

The first step in the preparation of this solution is to dissolve the salts; then hydrochloric acid is added, which liberates a definite quantity of bromin, as the equation illustrates:

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$

The stopper should be inserted into the bottle as soon as the hydrochloric acid has been added, in order that no bromin vapor escape, and the bottle rotated so as to mix the acid thoroughly with the liquid.

The next step is to determine the quantity of bromin which a definite volume of solution will liberate. The bromin solution should be of such strength that 1000 mils of it will

contain 7.976 gms. of available bromin. Bromin, like chlorin, liberates iodin from potassium iodid, and is estimated in the same manner.

One atomic weight of iodin is liberated by one atomic weight of bromin:

$$Br_2 + 2KI = 2KBr + I_2$$

Thus by determining the quantity of iodin liberated the quantity of bromin is found.

The iodin is determined by the $\frac{N}{10}$ sodium thiosulphate, one liter of which represents 12.692 gms. of iodin, which is equivalent to 7.992 gms. of bromin, as shown by the following equation:

$$\underset{20)159.84}{(Br_2)} = \underset{20)253.84}{I_2} + \underset{20)496.44}{2(Na_2S_2O_3 + 5H_2O)}$$

7.992 gms. 12.692 gms. 24.822 gms. or 1000 mils $\frac{N}{10}$ V.S.

$$= 2NaI + Na_2S_4O_6 + 10H_2O.$$

The Assay of Phenol. Dissolve 1 gm. of the sample in sufficient water to make 500 mils of solution at the standard temperature. Twenty mils of this solution containing 0.04 gm. of the sample are transferred to a glass-stoppered bottle, having a capacity of about 200 mils.

To this, 30 mils of decinormal bromin, followed by 5 mils of hydrochloric acid, are added, and the bottle immediately stoppered, and shaken repeatedly during half an hour.

Then the stopper is removed just sufficiently to introduce 5 mils of a 20 per cent aqueous solution of potassium iodid, being careful that no bromin escape.

The bottle is then thoroughly shaken and the neck rinsed with a little water, the washings being allowed to flow into the bottle, then 1 mil of chloroform is added, the mixture thoroughly

shaken, and titration with decinormal sodium thiosulphate V.S. begun, starch being used as indicator, until the blue color is just discharged.

The precipitated tribromphenol interferes somewhat with the end-reaction when starch is used, and frequently with old phenol solutions * the precipitate possesses a bluish color which is not removed by an excess of sodium thiosulphate and which makes the end-reaction difficult. This difficulty is overcome by the use of a small quantity of chloroform which dissolves the tribromphenol and admits of a very sharp end-reaction.

When chloroform is alone used, the end-reaction is very clearly defined, and is known by a colorless aqueous solution and the chloroform being free from any tinge of pink, due to traces of iodin.

Note the number of mils of $\frac{N}{10}$ thiosulphate used; deduct this number from 30 mils (the quantity of $\frac{N}{10}$ bromin originally added), and the quantity of $\frac{N}{10}$ bromin which went into combination with the phenol is obtained.

Each mil of $\frac{N}{10}$ bromin represents 0.001556 gm. of pure phenol.

Example. Assuming that 6 mils of $\frac{N}{10}$ sodium thiosulphate were required to discharge the color of the starch iodid, this deducted from 30 mils leaves 24 mils, the quantity which combined with the phenol.

$$0.001566 \times 24 = 0.037584 \text{ gm.}$$

$$\frac{0.037584 \times 100}{0.04} = 93.96 \text{ per cent of pure phenol.}$$

* F. X. Moerk, A. J. Ph., 1904, 475.

The above method originated with Koppeschaar, and is the only volumetric method by which accurate results may be obtained.

It is based upon the fact that bromin reacts with phenol, producing an insoluble precipitate of tribromphenol.

The titration is not made directly; but the phenol solution is treated with an excess of standard bromin solution in the presence of some hydrochloric acid. The hydrochloric acid liberates the bromin, and the freed bromin reacts with the phenol, as shown by the equations:

(*a*) $5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3H_2O + 3Br_2$

(*b*) $C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$

$6)94$ $\quad$ $6)479.92$

$10)15.66$ $\quad$ $10)79.92$

1.566 gms. $\quad$ 7.992 gms. or 1000 mils $\frac{N}{10}$ bromin V.S.

Thus each mil of the $\frac{N}{10}$ bromin represents 0.001566 gm. of pure phenol.

The bromin solution which was added in excess, and the liberated bromin of which is not fixed by phenol, is then found by residual titration with $\frac{N}{10}$ sodium thiosulphate after the addition of some potassium iodid.

The decinormal bromin solution and the decinormal sodium thiosulphate solution being equivalent, each mil of the latter consumed represents one mil of the former. Then by subtracting the number of mils of the sodium thiosulphate solution from the number of mils of bromin solution originally added, the quantity of the latter which was actually consumed by the phenol present is found. This number, when multiplied by the factor for phenol, then gives the quantity of pure phenol present.

The hydrochloric acid used in the above estimation must contain no free chlorin. The potassium iodid must be free from iodate. The starch T.S. should not be added until most of the free iodin has been taken up, and the color of the solution has diminished to light yellow.

The carbolic acid should be diluted with water before titration, and should never be stronger than 0.1 gm. in 25 mils.

Resorcinol, $C_6H_4(OH)_2$ 1 : 3 (110.05). Dissolve about 1.5 gm., accurately weighed, in sufficient distilled water to measure 500 mils. Transfer 25 mils of this solution (representing 0.075 gm.) to a 500-mil glass-stoppered flask, add 50 mils of decinormal bromin V.S., and dilute with 50 mils of distilled water. Then add 5 mils of hydrochloric acid and at once stopper the flask, shake well, dilute it with 20 mils of distilled water, add 5 mils of potassium iodid T.S., let stand five minutes, and then titrate the liberated iodin with decinormal sodium thiosulphate V.S., using starch as indicator.

Calculate as in preceding assay. Each mil of decinormal bromin corresponds to 0.001834 gm. of $C_6H_4(OH)_2$.

Phenylsulphonates, *Sulphocarbolates.* Dissolve about 0.25 gm. of the salt, accurately weighed, in 50 mils of distilled water, add 50 mils of decinormal bromin V.S. and 5 mils of hydrochloric acid. Allow the mixture to stand for fifteen minutes, then add 2 gms. of potassium iodid dissolved in 5 mils of water, and titrate the liberated iodin with decinormal sodium thiosulphate V.S., using starch as indicator.

Each mil of decinormal bromin V.S. used corresponds to 0.04903 gm. of $NaC_6H_5O.SO_3$.

CHAPTER XIV

SOME TECHNICAL EXAMINATION METHODS FOR FATS, OILS AND WAXES

The Acid Value or Proportion of Free Fatty Acids. This indicates the number of milligrams of KOH required to neutralize the free fatty acids in 1 gm. of oil, fat or wax. This standard alkali used is in alcoholic solution and may be $\frac{N}{2}$, $\frac{N}{5}$, or weaker, depending upon the nature of the fat. Phenolphthalein is the indicator. The fat is dissolved, according to Geissler, in ether, but alcohol or purified methylated spirit, chloroform or a mixture of alcohol and ether may be used. The solvent, whichever is used, must be free from acidity, and should be neutralized with $\frac{N}{10}$ alkali if necessary.

The Process. Ten gms. of the oil are accurately weighed into a flask and about 50 mils of solvent added. A few drops of phenolphthalein are then added and the titration with alcoholic $\frac{N}{2}$ potassium hydroxid solution begun, shaking constantly until the first appearance of a pink color. Care must be taken not to add too great an excess of the alkali, otherwise saponification will occur. A small excess may, however, be added and retitrated with standard acid; a more distinct end-point is then obtained. In the case of waxes or solid fats, the solvent is added, heat applied until it boils, and the titration at once started.

One mil of $\frac{N}{2}$ KOH = 0.02805 gm. of KOH or 28.05 mgms.

The number of mils used, multiplied by 28.05 and then divided by the weight of oil taken, gives the milligrams of KOH neutralized by the free fatty acids of the oil, i.e., the acid value.

The Saponification Value (Köttstorfer Number).* This indicates the number of milligrams of KOH required for the complete saponification of one gram of fat or oil. Reagents required are:

Alcoholic Potassium Hydroxid Solution, made by dissolving 40 gms. of potassium hydroxid in 1 liter of 95 per cent alcohol.

Half-Normal Hydrochloric Acid Solution. Each mil of which = 28.05 mgms. of KOH.

Indicator. Phenolphthalein 1 gm. in 100 mils of 95 per cent alcohol.

The Process. Into an Erlenmeyer flask capable of holding 200 mils, accurately weigh about 1.5 gms. of the fat (previously purified and filtered). Run into this from a burette 25 mils of the alcoholic potassium hydroxid solution. Then insert into the neck of the flask a perforated stopper provided with a glass tube 70 to 80 cm. in length and from 5 to 8 mm. in diameter, and set it in a water-bath for half an hour or until the fat is entirely saponified. The operation is facilitated by occasional agitation. The flask is then removed, its contents cooled and titrated with the half-normal hydrochloric acid, using phenolphthalein as indicator. The alcoholic potassium hydroxid solution is standardized by conducting a blank experiment similar in every detail to the above with the exception that the fat is omitted.

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* J. Köttstorfer, 1879, Zeitschr. anal. Chem., XVIII, 199.

The Köttstorfer number is then ascertained by subtracting the number of mils of the standard hydrochloric acid used in the analysis from the number necessary to neutralize 25 mils of the alcoholic potassium hydroxid solution in the blank experiment, multiplying the difference by 28.05 and dividing by the weight of fat taken.

Example. 1.5 gms. of the fat was treated with 25 mils of alcoholic potassium hydroxid solution, under the above described conditions, and in titrating the excess, 21.5 mils of $\frac{N}{2}$ hydrochloric acid was required. In the blank experiment 25 mils of the alcoholic potassium hydroxid required 32 mils of the $\frac{N}{2}$ acid. Then $32-21.5=10.5$.

$$\frac{10.5\times 28.05}{1.5}=196.$$

196 is the milligrams of KOH neutralized by 1 gm. of the oil, or the Köttstorfer saponification number.

TABLE SHOWING REQUIREMENT AS TO SAPONIFICATION NUMBER

Lard oil	195 to 197	Olive oil	191 to 195
Almond oil (expressed)	191 to 200	Castor oil	179 to 180
Cottonseed oil	191 to 196	Theobroma oil	188 to 195
Linseed oil	187 to 195	Croton oil	212 to 218
Cod-liver oil	175 to 185	Yellow wax	90 to 96

The Reichert Number or Volatile Fatty Acid Value. This indicates the number of mils of decinormal KOH required to neutralize the volatile fatty acids distilled from 2.5 gms. of fat. This method is conducted as follows: 2.5 gms. of the clear filtered fat are taken in an Erlenmeyer flask of about 150 mils capacity with 1 gm. of potassium hydroxid and 20 mils

of 80 per cent alcohol, and the whole digested on a water-bath (rotating the flask frequently) until saponification is complete and the alcohol all removed. 50 mils of water are then added, and 20 mils of dilute sulphuric acid (1:10) and the mixture distilled. The distillate is collected in a 50-mil flask into which is set a funnel with a wetted filter to collect any insoluble fat acid. The first 10 or 20 mils of distillate are returned to the flask, and the 50 mils distilled. This is treated with a few drops of phenolphthalein and then titrated with decinormal potassium hydroxid. The number of mils consumed is the Reichert Number.

In the Meissl modification (the Reichert-Meissl method) 5 gms. of the fat are taken and a more complete distillation of the volatile acids effected. The method is particularly useful in determining the genuineness and purity of butter.

The Reichert-Meissl Number. This is undoubtedly the best process for detecting the admixture of foreign fats with butter. This process depends upon the fact that butter contains certain constituents which, when appropriately treated, yield volatile acids in much larger quantity than is obtained from any of the practicable substitutes for butter. These acids are principally butyric and caproic. The process consists in saponifying the fat with an alkali, then separating the fatty acids by neutralization, and distilling off the volatile acids for titration with standard alkali.

The operations involved in this process do not admit of any arbitrary variation, and reliable and comparable results can only be obtained by strictly adhering to the prescribed details.

The following process is adopted by the Association of Official Agricultural Chemists. The solutions required are:

Sodium Hydroxid Solution. One hundred gms. of sodium hydroxid are dissolved in 100 mils of distilled water. The

alkali should be as free as possible from the carbonates, and be preserved out of contact with the air.

Potassium Hydroxid Solution. One hundred gms. of the purest potassium hydroxid are dissolved in 58 mils of hot distilled water, cooled in a stoppered vessel, and the clear liquid decanted and preserved out of contact with the air.

Sulphuric Acid. Mix 200 mils of the strongest acid with 1000 mils of water.

Alcohol of about 95 per cent, redistilled from caustic soda.

Standard Barium Hydroxid Solution, accurately standardized, approximately decinormal.

Indicator. Dissolve 1 gm. of phenolphthalein in 100 mils of 95 per cent alcohol.

The process:

Weighing the Butter. The butter to be examined should be melted and kept in a dry, warm place at about 60° C. for two or three hours, until the water and curd have entirely settled out. The clear supernatant fat is poured off and filtered through a dry filter-paper in a jacketed funnel containing boiling water. Should the filtered fat in a fused state not be perfectly clear, it must be filtered a second time. This is to remove all foreign matter and any trace of moisture. The saponification flasks are prepared by thoroughly washing with water, alcohol and ether, wiping perfectly dry on the outside, and heating for one hour at the temperature of boiling water. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within fifteen or twenty minutes of the time they are weighed. The weight of the flasks having been accurately determined, they are charged with the melted fat in the following way:

A pipette with a long stem, marked to deliver 5.75 mils,

is warmed to a temperature of about 50° C. The fat, having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, is then taken up in the pipette and the nozzle of the pipette carried nearly to the bottom of the flask, having been previously wiped to remove any adhering fat, and 5.75 mils of fat are allowed to flow into the flask. After the flasks have been charged in this way they should be recovered with the silk handkerchief, allowed to stand fifteen or twenty minutes, and again weighed.

The Saponification. Three methods may be employed:

1. *Under Pressure with Alcohol.* Ten mils of 95 per cent alcohol are added to the fat in the flask, and then 2 mils of the caustic soda solution. A soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water or steam bath (see Fig. 55). The flask during the saponification, which should last one hour, should be gently rotated from time to time, being careful not to project the soap for any distance up its sides. At the end of an hour the flask, after having been cooled nearly to room temperature, is opened.

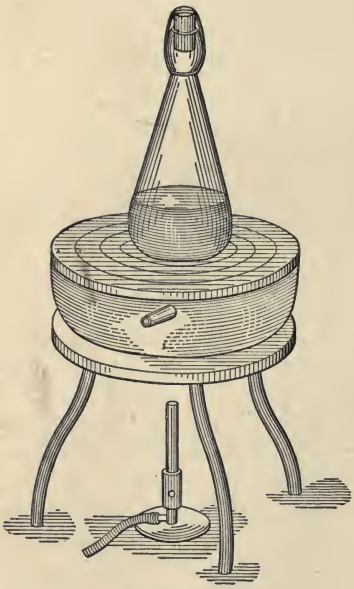

Fig. 55.

2. *Under Pressure without the Use of Alcohol.* Place 2 mils of the potassium hydroxid in the flask containing the fat, which must be round-bottomed and made of well-annealed

glass to resist the pressure; cork, and heat as in the previous method. Rotate the flask very gently during the saponification, taking great care that none of the fat rises on the sides of the flask out of reach of the alkali. Potash makes a softer soap than soda and thus allows a complete saponification without the use of alcohol. This method avoids the danger of formation of esters and the trouble of removing the alcohol after saponification.

3. *With a Reflux Condenser and the Use of Alcohol.* Place 10 mils of the 95 per cent alcohol in the flask containing the fat, add 2 mils of the sodium hydroxid solution with a reflux condenser (a glass tube not less than 1 meter in length is allowable) and heat on the steam bath until the saponification is complete.

Removal of the Alcohol. The stoppers having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into a steam bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and to avoid any loss from this cause or any creeping of the soap up the sides of the flask, it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro, or better, by a current of carbon dioxid free air.

Dissolving the Soap. After the removal of the alcohol the soap should be dissolved by adding 135 mils of recently boiled distilled water (or 132 mils if potassium hydroxid was used in the saponification), warming on the steam bath, with occasional shaking until solution of the soap is complete.

Setting Free the Fatty Acids and Distilling. Cool to from 60° to 70° C., throw in a few pieces of pumice stone, add 5 mils of the dilute sulphuric acid (or 8 mils if potassium hydroxid

was used in the saponification), stopper as in the method of saponification, and heat on the water-bath until the fatty acids form a clear, transparent layer on top of the water. This may take several hours. Cool to room temperature, add a few pieces of pumice stone, and connect with a glass condenser, as in Fig. 56.

Heat slowly with a naked flame until ebullition begins, and distil, regulating the flame in such a way as to collect 110 mils of distillate in as nearly thirty minutes as possible.

Mix this distillate, filter through a dry filter, and titrate 100 mils with the standard barium hydroxid solution, using

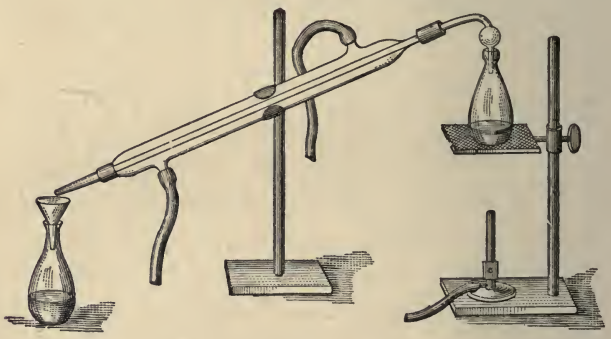

Fig. 56.

0.5 mil of phenolphthalein as indicator. The red color should remain unchanged for two or three minutes.

Increase the number of cubic centimeters of tenth-normal alkali used by one-tenth, divide by the weight of fat taken, and multiply by five to obtain the Reichert-Meissl number. Correct the result by the figure obtained in a blank experiment.

When treated as above described, 5 gms. of genuine butter never yields less acidity than is represented by 24 mils of $\frac{N}{10}$

alkali. It is true, however, that the butter made from the milk of a single cow, especially towards the end of her period of lactation, has been known to fall slightly below this figure, but the average butter, as produced from the mixed milk of a herd, usually requires 27 mils or more. Oleomargarin requires about 1 mil of beef-fat, and lard about the same. Cacao butter requires about 7 mils.

The percentage of butter-fat in a mixture of fats, 5 gms. being taken: $(n - 0.6) \times 3.65$ = percentage of true butter-fat.

Iodin Absorption Number of Fats and Oils (Hübl's Number.)* This is the percentage of iodin absorbed by a fat or an oil under certain conditions. In other words it is the number of parts of iodin absorbed by 100 parts of an oil.

Reagents required:

(*a*) **Hübl's Iodin Solution.** Dissolve 25 gms. of pure iodin in 500 mils of alcohol, and mix this solution with 500 mils of alcohol containing 30 gms. of pure mercuric chlorid, and set aside for twenty-four hours. The mercuric chlorid solution should be filtered if necessary before it is mixed with the alcoholic iodin solution. This solution loses its strength rapidly, and should therefore be tested before using.

(*b*) Decinormal sodium thiosulphate.

(*c*) Potassium iodid solution, 20 gms. in 100 mils.

(*d*) Starch paste indicator.

The Process. To about 0.3 gm.† of the fat or oil, accurately weighed and dissolved in 10 mils of chloroform, con-

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* Dingler's Polyt. Jour., 1884, 281; Am. Ch. Jour., VI, 285.

† In the case of drying oils which have a very high absorbent power, as linseed oil, use from 0.15 to 0.20 gm.; for oil of theobroma and similar fats use 0.80 gm.

tained in a glass-stoppered bottle of 250 mils capacity, add 25 mils of the iodin solution. Stopper the bottle securely and place in a cool, dark place for four hours.* At the expiration of this time, the mixture must still possess a brown color; if it does not, a further measured quantity of the iodin solution must be added and the mixture again set aside. Finally 20 mils of the potassium iodid solution are added together with 50 mils of water, and the mixture titrated with the decinormal sodium thiosulphate until the color is almost discharged, when a few drops of starch indicator are added and the titration continued until the solution is colorless.

The Standardization of the Iodin Solution is effected by subjecting it to the same treatment as in the assay, but with the oil omitted, and at the end of four hours titrating with the decinormal thiosulphate.

The difference between the number of mils of thiosulphate solution used in the blank test and the number used in the actual assay, is multiplied by 12.59, and this divided by 3, gives the iodin value of the oil under analysis.

When the quantity of the oil or fat taken is not 0.3 gm., then the product is not divided by 3, but by the figure corresponding to the quantity taken; thus if 0.15 gm. are taken the product is divided by 1.5.

Another way of making the calculation is as follows:

The difference between the mils of thiosulphate used in the blank test and the mils used in the analysis, is multiplied by 0.01259, then by 100, and the product divided by the weight in grams of the oil taken for analysis.

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* The time allowed does not give the complete iodin absorption power of an oil or fat and cannot be compared with determinations in which six to twelve hours have been used. It gives, however, very satisfactory comparative results, but the time factor must be very closely observed.

Example:

Number of mils of thiosulphate used in blank test..... 45.4
" " " " " " " analysis..... 26.1

" " " " representing iodin absorbed..... 19.3

Iodin number is $\frac{19.3 \times 0.01259 \times 100}{0.3} = 80.9$.

This method, as is well known, is based upon the fact that the unsaturated glycerids in the oils form addition products with the iodin. The mercuric chlorid and iodin contained in the alcoholic solution interact with a formation of mercuric chloriodid and iodin chlorid; the latter is supposed to be the active agent.

$$HgCl_2 + I_2 = HgClI + ICl.$$

The mercuric chlorid also acts the part of a carrier of halogen similar to that played by mercury in the Kjeldahl process when dissolving the substance in sulphuric acid.

Gill and Adams, J. A. C. S., XXII, 12, call attention to the fact that not only addition products, but also substitution products, are formed in this process, which vary in amount with the time of action and the strength of the solution. This is a feature which interferes with the accurate determination of the iodin number, giving as it does a higher figure. In order to prevent this formation of substitution products, and thus overcome the discrepancy in results, these authors suggest the use of mercuric iodid instead of mercuric chlorid, making the solution with methyl alcohol (free from acetone and anhydrous). They claim that by the use of a solution so made a truer iodin absorption number is obtained. A great disadvantage of the Hübl method is that the solution quickly loses its strength; another is, the length of time required

for the absorption. As above described, four hours are required, but this is not sufficient time to allow of complete absorption of the iodin. It is, however, a good practice to have a fixed time limit; the process then gives very satisfactory comparative results.

Iodin Absorption Number. The Hanus Method.* This method is conducted like the foregoing. It differs in the composition of the iodin solution used. This is prepared as follows: Dissolve 13.2 gms. of powdered iodin in 1000 mils of pure glacial acetic acid with the aid of gentle heat if necessary, to facilitate solution. Cool to 25° C. and determine the iodin content in 20 mils of the solution by means of decinormal sodium thiosulphate V.S.; then add to the solution a quantity of bromin, molecularly equivalent to that of the iodin present (3 mils is the usual approximate amount). Keep the solution in glass-stoppered bottles protected from light.

The Process. Introduce about 0.8 gm. of a solid fat or 0.3 gm. of an oil, accurately weighed, into a glass-stoppered bottle of 250 mils capacity. Dissolve it in 10 mils of chloroform, add 25 mils of the iodin solution, stopper the bottle securely, and allow the mixture to stand for half an hour in a cool, dark place. After this time it must still retain a brown color; if it is not brown, a new test should be started using a smaller quantity of the fat or oil. Then add in the order named, 30 mils of potassium iodid T.S., 100 mils of distilled water, and decinormal sodium thiosulphate V.S. in small successive portions, shaking thoroughly after each addition, until the color of the mixture becomes quite pale. Then add a few drops of starch solution and continue the addition of the thiosulphate V.S. until the blue color is discharged. Then make a blank test by mixing exactly the same quantities

* Zeitschr. Nahr. u. Genus. (1901), 913.

of the iodin solution and chloroform, and titrating the free iodin with thiosulphate V.S. as directed above. The difference in the number of mils of the thiosulphate V.S. consumed in the blank test and the actual test multiplied by 1.269 and divided by the weight of the fat or oil taken gives the iodin number.

In the case of oils which have a high iodin-absorbing power, smaller quantities of the oils should be used. 0.15 to 0.18 gm. for linseed oil and about 0.2 gm. for cod liver oil. The time allowed for absorption in the case of castor oil and linseed oil should be one hour.

The consensus of opinion among chemists is that the Hanus method is the most satisfactory. Its principal advantage over the Hübl method lies in the facts (*a*) that the Hanus iodin solution is much more stable, (*b*) that the time required for the reaction is comparatively much shorter.

TABLE SHOWING IODIN ABSORPTION NUMBER FOR SOME COMMON OILS

	Hübl's No. Four Hours.	Hanus' No. Half an Hour.
Almond oil (expressed)	98.2	98.7
Butter	35.4	35.4
Castor oil	87.3	87.5
Cocoanut oil	8.4	8.6
Cod liver oil	144.3	143.9
Cottonseed oil	104.3	106.6
Lard oil	69.5	69.7
Linseed oil	179.6	186.2
Mustard oil	113.1	115.3
Olive oil	86.1	86.8
Oleomargarin	52.1	52.3
Peanut oil	96.3	97.3
Rape oil	102.4	105.2
Sesame oil	106.4	106.5
Theobroma oil	35.4	35.5

The Acid Number for Resins. This is the number of milligrams of potassium hydroxid required to neutralize 1 gm. of a resinous substance.

The Process. About 2 gms. of the resinous substance, accurately weighed, is dissolved in alcohol, and the solution titrated with half-normal potassium hydroxid V.S., using phenolphthalein as indicator. The number of mils of the half-normal alkali V.S. required for neutralization when multiplied by 0.028055 and the product divided by the weight, gives the acid number of the resin.

CHAPTER XV

ESTIMATION OF SUGARS

Preparation of Fehling's Solution. (*a*) *The Copper Solution.* 34.66 gms. of carefully selected small crystals of pure cupric sulphate are dissolved in sufficient water to make, at or near 25° C., exactly 500 mils. Keep in small well-stoppered bottles.

(*b*) *The Alkaline Tartrate Solution.* 173 gms. of potassium and sodium tartrate (Rochelle salt) and 75 gms. of potassium hydroxid are dissolved in sufficient water to make, at or near 25° C., exactly 500 mils. Keep in small rubber-stoppered bottles.

For use, equal quantities of the two solutions should be mixed at the time required.

One molecular weight of water-free glucose will reduce five molecular weights of cupric oxid, i.e., 180.12 gms. of glucose will reduce 1248.7 gms. of crystallized copper sulphate ($CuSO_4+5H_2O$). If pure chemicals are used in the preparation of this solution there will be no need of standardizing it, but if the solution is old and its titer doubtful, the following method of standardization may be employed.

The Standardization. Dissolve 0.95 gm. of pure cane sugar in 50 mils of water, add 2 mils of hydrochloric acid, and heat to 70° C. for ten minutes. Then neutralize with sodium carbonate and dilute to 1 liter.

Fifty mils of this solution should exactly reduce 10 mils of Fehling's solution, when treated as described below.

Ten mils of the mixed Fehling's solution is equivalent to

Glucose	0.050 gm.
Maltose	0.0806 "
Inverted cane-sugar	0.0475 "
Inverted starch	0.045 "
Lactose	0.0678 "

Estimation of Reducing Sugars. (*Glucose, Maltose, Inverted Cane-sugar, Lactose and Inverted Starch.* 0.5 gm. or less of the sugar is dissolved in 100 mils of distilled water, and put into a burette. Ten mils of the mixed Fehling's solution, accurately measured, is put into a 100-mil Erlenmeyer flask, or in a white porcelain dish, diluted with 40 mils of distilled water, and rapidly heated to boiling. The solution should remain perfectly clear and retain its blue color. If it does not it should be rejected.

The hot, clear blue solution is immediately titrated with the sugar solution, which should be added in small portions at a time, boiling after each addition until the copper is completely precipitated and the blue color of the solution is entirely destroyed. The solution is then boiled about two minutes longer, and the amount of the sugar solution used is read off.

The Calculation. Ten mils of Fehling's solution are always taken; and whatever the quantity of glucose or other sugar solution is required to effect its complete reduction, that quantity contains the equivalent of 10 mils of Fehling's solution, as shown in the table above.

Thus if 12 mils of the sugar solution were required to reduce 10 mils of Fehling's solution, the 12 mils contain 0.05 gm. of glucose or 0.0806 gm. of maltose, etc. One hundred mils of the solution therefore contain x gm. of glucose.

$$\frac{0.05 \times 100}{12} = 0.416 \text{ gm. glucose.}$$

In order to obtain reliable results it is important that the process be carried out exactly as laid down in the above directions, and that the quantity of sugar present in solution be no greater than one per cent. The degree of heat and the time occupied in the process, as well as the concentration of the Fehling's solution, have a very important bearing upon the accuracy of the results.

It is advisable to complete the titration in as short a time as possible. A preliminary test should always be made, in which the approximate quantity of the solution required is found; then a second and more accurate titration can be done in which the sugar solution may be added more boldly, and the time of boiling and exposure of the copper solution to the air much lessened. The complete reduction of the copper (using undiluted Fehling's), after the addition of the requisite quantity of sugar, does not take place instantly. The time required varies somewhat with the different sugars. For instance, with glucose, invert sugar and levulose, the reduction is not complete until after heating two minutes; with maltose four minutes, and with lactose six minutes are required.

If the sugar to be examined be either glucose, maltose, or lactose, it may be titrated directly; but if it be *sugar-cane*, it must first be inverted. This is done by dissolving the sugar (0.5 gm.) in about 100 mils of water, adding 3 or 4 drops of strong hydrochloric acid, and boiling briskly for ten or fifteen minutes. This is then allowed to cool, neutralized with potassium hydroxid, and made up to 100 mils with water.

The sugar in urine may be estimated by this process. The urine is placed in the burette and run into the boiling Fehling's solution in the usual manner. If it contain a large quantity of sugar, it must be diluted two or three times.

In estimating with Fehling's solution it is well to attach a

rubber tube eight to twelve inches in length to the lower end of the burette, so that the boiling need not be done directly under the burette, and thus cause incorrect readings through the expansion of the liquid therein.

Determination of the End-point. It is always somewhat difficult to determine the exact point at which the blue color disappears, owing to the presence of the precipitated suboxid of copper. This difficulty may be overcome by the addition of some substance which will prevent the precipitation of the cuprous oxid, such as ammonium hydroxid or potassium ferrocyanid. When the latter is used the disappearance of the blue color can then be readily seen, as the solution remains clear to the end, turning from blue to green, and finally brown, which indicates the end of the reaction.

Professor Bartley reports this method as accurate, reliable, and rapid, provided the solution be not boiled during the reduction. He recommends adding to the Fehling's solution in the porcelain basin 10 mils of a 10 per cent freshly prepared solution of potassium ferrocyanid and 30 mils of water. The ferrocyanid does not precipitate the copper in alkaline solution.

L. Beulaygue (Compt. rend., 138, 51) suggests the following method for determining the end-reaction when titrating sugar solution in the usual manner with Fehling's reagent, using solution of sodium monosulphid as the indicator. When the end of the reaction is near, a little of the hot solution is applied by means of a glass rod, to two superimposed white filter papers. The upper one acts as a filter, retaining the particles of cuprous oxid. The lower paper is withdrawn, and the moist spot touched with a drop of the sodium monosulphid reagent, when an immediate black stain of cupric sulphid is formed if the reaction is not complete. By successive spotting out and testing in this manner, a very accurate reading of the end-reaction may be obtained. It is important, when

standardizing the Fehling's solution, that the same indicator should be employed. Potassium ferrocyanid in solution, acidified by either hydrochloric or acetic acid, may be employed in a similar manner. The end-reaction in then indicated by the disappearance of the red color from the last spot.

E. F. Harrison,* who has employed Fehling's solution somewhat extensively in quantitative sugar estimations, has found the indicators usually recommended to determine the end-point of reaction to be unsatisfactory. It was suggested by him that the action of cupric salts in liberating iodin from iodid might be utilized for this purpose with advantage, and his experiments determine the superiority of this over the other indicators heretofore proposed. The indicator is prepared by boiling 0.05 gm. of starch with a few mils of water, adding 10 gms. of potassium iodid and diluting to 100 mils. This indicator should be prepared as required. In use 0.5 to 1.0 mil of this solution is acidified with about 5 or 10 drops of acetic acid, and one drop or more of the liquid in process of titration added. As long as unreduced copper is present, a color is produced, varying from red to blue, and of greater or less intensity, according to the nearness of the end-point. The production of no color marks the end of the reaction. The indicator is available with one drop of a solution containing one part of cupric sulphate in twenty thousand parts.

Estimation of Maltose in Malt Extract. A half per cent solution of the sample is prepared, and titrated into 10 mils of Fehling's solution in the manner described above.

Estimation of Starch After Inversion. This method consists in converting the starch into glucose and then estimating the glucose with Fehling's solution.

Two gms. of the starch are mixed with water, and boiled

* Trans. Brit. Ph. Conf., 1903, 568–9.

for fifteen minutes; the solution is then cooled, and diluted to about 200 mils. Eighteen mils of strong hydrochloric acid are then added, and the solution heated under a return condenser for two or three hours. The solution is then cooled, neutralized with potassium hydroxid and diluted to 250 mils. This is put into a burette and titrated into 10 mils of Fehling's solution, as described above, under reducing sugars.

In estimating the starch in baking powder, 2 to 5 gms. of the powder are introduced into an Erlenmeyer flask, 150 to 200 mils of a 4 per cent solution of hydrochloric acid are added and the solution gently boiled for four hours, after which the flask and contents are cooled, neutralized by adding sodium hydroxid, and made up to a definite volume. It is then ready for testing with Fehling's solution.

Ten mils of Fehling's solution is the equivalent of 0.0475 gm. of invert starch.

Estimation of Starch after Inversion by Means in Diastase. The treatment of starch with malt infusion or pure diastase at a temperature not above 70° C., readily converts the starch into maltose, but the solution also contains, besides maltose, various dextrins in proportions varying with the temperature at which the diastase acts. The digestion may vary from fifteen minutes to fifteen hours. Complete conversion of the starch may be determined by testing occasionally with iodin. A blank experiment should be made, especially if the digestion is carried on beyond half an hour. A like quantity of the same diastase solution should be digested at the same temperature and for the same time, and the amount of sugar found deducted from the total quantity found in the analysis. Faulenbach * makes use of the following solution of diastase: Crush 3.5 kilos of fresh green malt, treat with a mixture of two liters of water and four liters of glycerin and let stand

* Zeitschr. f. physiol. Chem., VII, 510; and Chem. Centralh., 1883, 632.

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for one week, stirring occasionally; then express and filter. This solution is very stable. Five drops of it will dissolve 1 gm. of starch; 15 drops of it contain a quantity of carbohydrate = 0.001 gm. of glucose.

A quantity of the substance to be tested (containing about 2 gms. of starch) is boiled to gelatinize the starch. Fifteen drops of the diastase solution are then added, and the mixture digested at 63° C. It is then filtered to separate the undissolved cellulose, etc., and heated with 20 mils of hydrochloric acid in a water-bath for three hours. The acidity is then just destroyed by means of caustic soda, the glucose determined, 0.001 gm. deducted, and the starch calculated from the glucose.

O'Sullivan * employs pure diastase, prepared as follows: Pour sufficient water over 2 or 3 kilos of finely crushed pale malt to just cover it. Let stand for three or four hours, then express and filter the solution. Add alcohol (sp.gr. 0.83) until the liquid above the flocculent precipitate becomes opalescent. Collect the precipitate, wash it with alcohol (sp.gr. 0.86 to 0.88) then with absolute alcohol and press it between linen. Finally dry it in a vacuum over sulphuric acid.

Estimation of the Diastasic Value of Malt Extract. The diastasic value of malt extracts may also be determined by estimating the amount of maltose produced by a given amount of the extract in a given time, when brought in contact with an excess of gelatinized starch solution. It is always necessary to estimate the copper-reducing power of the extracts with Fehling's solution upon a separate sample, and to deduct this from the total reducing power found after treatment with the starch.

The process is briefly as follows: A definite quantity (say 30 mils) of gelatinized starch, made from the best Bermuda

* Jour. Chem. Soc., XLV (1884), 1.

arrowroot, of 3 per cent strength, is placed in a flask and heated to 40° C. A weighed amount of the malt extract (say 20 mils of a 1 per cent solution) is then added, and the temperature kept at 40° C. for exactly half an hour. At the end of this time some sodium hydroxid solution is added in order to check the further action of the diastase upon the starch (heating to 100° C. accomplishes the same result). The solution is then diluted to a definite volume with water and the maltose produced, estimated by Fehling's solution in the usual manner. The quantity of reducing sugar originally present in the sample must be previously determined, and this amount deducted from the total amount found after treatment with starch, and the remainder calculated as maltose. Ten mils of Fehling's solution is the equivalent of 0.0806 gm. of maltose.

CHAPTER XVI

ESTIMATION OF FORMALDEHYDE*

The Ammonia Method (Legler). This method is based upon the reaction between free ammonia and formaldehyde in which hexamethylene-tetramin is formed. It is for ordinary purposes sufficiently accurate.

It is this method which is recommended by Lederle † for use in the laboratory of the New York City Health Department, and by Prescott in the laboratory of the Universtiy of Michigan.

The assay is conducted as follows: 2 mils of the solution are placed in a glass-stoppered bottle, the stopper of which is thickly coated with petrolatum, and 50 mils of $\frac{N}{2}$ ammonia solution added; let stand twelve hours, shaking occasionally. Then determine the excess of ammonia by titrating with $\frac{N}{2}$ sulphuric acid solution, using rosolic acid or litmus as indicator. The excess of ammonia subtracted from the quantity added gives the quantity which combined with the formaldehyde, and thus the amount of the latter is ascertained.

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* Berichte d. Chem. Ges., XVI., 1335, 1883.

† Am. Drug., 1897, 246.

The reaction is represented as follows:

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

4)180 4)68.04 Hexamethylenetetramin

2)45 2)17.01

22.5 gms. 8.5 gms. or 1000 mils $\frac{N}{2}$ V.S.

0.0225 gm. 0.0085 gm. or 1 mils " "

Assuming that 22 mils of $\frac{N}{2}$ sulphuric acid were employed in the titration, 22 mils of the $\frac{N}{2}$ ammonia solution must have been in excess, hence 28 mils of the latter went into combination with the formaldehyde. Thus the 2 mils of formaldehyde solution contained $28 \times 0.0225 = 0.63$ gm.

A. G. Craig* says that the chief difficulty in using the Legler method is the volatility of the ammonia. The difficulty is not so much the loss of strength in the standard solution, but the loss during the determination. He proposes the following scheme by which this error is removed.

Prepare a normal solution of sulphuric acid. Make up an approximately normal solution of ammonia, the exact strength being immaterial. Procure several three-ounce prescription bottles with smooth sides and close-fitting soft rubber stoppers. Prepare a methyl orange solution. Procure a boiler in which the bottles may be immersed to the neck without upsetting (a large beaker will do). Take as much of the sample as will contain 0.5 gm. of formaldehyde. Measure with the pipette, 25 mils of the ammonia solution into each of the bottles, and to half of them add a sample of formaldehyde; stopper tightly. If the necks of the bottles are small, the stoppers need not be tied down. Place the bottles in the boiler, add cold water to the necks, and heat to boiling. Boil for one

* J. A. C. S., XXIII, 642 (1901).

hour, and cool by running in cold water slowly, being careful not to allow the cold water to touch the hot bottles. Titrate with sulphuric acid and methyl orange *to the first indication of a color change.* Take the difference between the readings for the blanks and those for the samples, as the ammonia consumed in normal mils. Of this difference, 1 mil = 0.0601 gm. of formaldehyde.

The Legler method is also liable to error because the compound formed is a weak base, and as such combines with acid, while at the same time it is liable to decompose into ammonia and formaldehyde and thus give an indefinite end-point when the residual ammonia is titrated with acid. Error is also liable to be introduced, through the presence of carbonic acid in the ammonia water, which, with the indicator rosolic acid, gives no sharp end-reaction.

The Ammonium Chlorid Method. In this method a solution of ammonium chlorid is used, from which ammonium is evolved by treatment with sodium hydroxid. The excess of alkali is then determined by titration with standard solution of sulphuric acid. This method, as devised by H. Schiff,* and Modified by C. A. Male,† is as follows:

Introduce 2 gms. neutral ammonium chlorid, dissolved in 20 mils of water, into a flask or bottle of about 200 mils capacity, having a well-fitting stopper. Dilute 10 mils of the formaldehyde solution to 100 mils with water, and neutralize with sodium hydroxid solution, as the formaldehyde solution generally contains varying quantities of formic acid. Add 20 mils of this neutralized solution to the ammonium chlorid solution, then 25 mils of $\frac{N}{1}$ NaOH, and immediately stopper the flask, and

* Chem. Ztg., XXVII, 14 (1903).

† Pharm. Jour., June, 1905, 844. See also Carl E. Smith, A. J. Ph., LXX, 86, (1898).

leave for one hour. Afterwards determine the excess of alkali with $\frac{N}{2}$ H_2SO_4, using rosolic acid or litmus solution as indicator, both of which give up a sharp end-reaction. The reaction and calculation is based upon the following equation:

$$2NH_4Cl + 3CH_2O + 2NaOH = N_2(CH_2)_3 + 2NaCl + 5H_2O.$$

1 mil $\frac{N}{1}$ NaOH is equivalent to 0.045 gm. of formic aldehyde. This modified method is quite as simple, and gives results practically identical with that of Romijn.

Oxidation by Hydrogen Dioxid (Blank and Finkenbeiner) * This method depends upon the use of hydrogen dioxid for oxidizing formaldehyde into formic acid, in alkaline solution. The formic acid so produced neutralizes a portion of the alkali, and the excess of the latter is then determined by titration with standard acid. The method gives good results and can be very rapidly carried out.

Three mils of the formaldehyde solution are placed into a 100-mil Erlenmeyer flask, the latter closed with a well-fitting stopper, and the weight of the solution carefully taken. 50 mils of normal NaOH V.S. are then added, and followed immediately, but slowly, through a small funnel, by 50 mils of a 3 per cent hydrogen dioxid solution, previously neutralized with normal NaOH V.S., using a drop of litmus solution. The solution is allowed to stand about 15 minutes, or until the reaction has ceased. The funnel and the sides of the vessel are then rinsed with distilled water, a few drops of litmus solution added and the unconsumed alkali titrated with normal H_2SO_4 V.S. The mils of the latter deducted from the 50 mils of normal NaOH V.S. originally taken gives the quantity of the

* Berichte d. Chem. Ges., XXXI, 2979 (1898); and A. J. Ph., 1899, 486.

alkali V.S. which was consumed in the reaction. The difference multiplied by 0.03 gm. gives the weight of CH_2O in the sample. To find per cent multiply the result by 100 and divide by the weight of sample taken for analysis.

In the original process, double normal sodium hydroxid is used.*

The reaction is as follows:

$$CH_2O + H_2O_2 + NaOH = NaCOOH + 2H_2O$$

H_2O_2 oxidizes formaldehyde to formic acid, HCOOH, which reacts with and neutralizes NaOH.

The Iodometric Method (Romijn).† This method, which is considered the most rapid, most accurate, and most readily applied, depends upon the fact that iodin in the presence of an alkali acts as an indirect oxidizing agent, giving, when formaldehyde is present, the iodid of the base and formic acid:

$$CH_2O + I_2 + 2NaOH = 2NaI + CHOOH + H_2O.$$

As modified by L. Reuter ‡ it is as follows:

Twenty mils of 35 to 40 per cent formadlehyde are introduced into a graduated flask and distilled water added to bring up the volume to 500 mils. Of this thoroughly mixed fluid, 5 mils are introduced into a bottle capable of being perfectly closed. 30 mils of normal sodium or potassium hydroxid are added, and then $\frac{N}{5}$ iodin solution allowed to flow in from a burette with constant agitation, until the fluid remains a bright yellow color (36–60 mils). The shaking is then vigorously continued for one minute, when 40 mils of normal

* See C. Allen Lyford, J. A. C. S., XXIX, 1227 (1907) "The Action of Barium Peroxid and Hydrogen Peroxid upon Formaldehyde."

† Zeitschr. anal. Chem., XXXVI, 18–24 (1897); *ibid*, XXXIX, 60–63 (1900).

‡ Ph. Rev., 1903, 207.

sulphuric acid are added, and then the excess of iodin titrated with decinormal thiosulphate solution. Each mil of $\frac{N}{10}$ iodin solution consumed corresponds to 0.0015 gm. formaldehyde. A blank titration should always be made.

A solution containing as much as 5 per cent may be accurately estimated by this method, provided not more than 2 gms. be taken. The method is, however, not accurate in the presence of other aldehydes. F. O. Taylor,* commenting upon this method, says that it is quite satisfactory, but that the quantities of formaldehyde and reagents used are unnecessarily large and cumbersome, and the method is hence modified by him as follows:

From a weighing bottle, consisting of a small Erlenmeyer flask, fitted with a perforated rubber stopper through which passes a dropper, and containing about 25 or 30 mils of the formaldehyde solution, weigh out accurately about 10 gms of the solution into a stoppered 500-mil flask and fill this to the mark with distilled water. For titration remove 5 mils of this solution, corresponding to 0.1 gm. of the weighed quantity of formaldehyde, and put into a 200-mil Erlenmeyer flask. Into another flask put 5 mils of water for a blank titration. To both now add 20 mils of normal NaOH and then 20 mils of an approximately $\frac{N}{5}$ iodin solution, whose exact strength need not be known, and let stand for five or ten minutes for the entire completion of the reaction. Now add 25 mils of normal H_2SO_4 and titrate the excess of iodin with $\frac{N}{10}$ $Na_2S_2O_3$. The difference between the mils of thiosulphate used on the assay and the mils of the blank is the number of mils of $\frac{N}{10}$ iodin

* Bull. Ph., Aug., 1903, 323.

consumed by the formaldehyde. Each mil of $\frac{N}{10}$ iodin so used equals 0.0015 gm. of CH_2O.

The Potassium Cyanid Method.* This method is especially applicable to solutions containing small quantities of formaldehyde. It depends upon the fact that potassium cyanid and formaldehyde combine to form an addition product, in which one molecule of potassium cyanid combines with one molecule of formaldehyde, as shown by the following equation:

$$CH_2O + KCN = N{\equiv}C{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}O{-}K.$$

In the estimation, the formaldehyde is mixed with a known quantity of potassium cyanid (in excess), the excess of the latter being determined by the use of standard silver nitrate solution, and thus the quantity of potassium cyanid, which combined with formaldehyde is found, and from this the quantity of formaldehyde is calculated.

The process is carried out as follows:† Ten mils of $\frac{N}{10}$ silver nitrate are treated with 6 drops of 50 per cent nitric acid in a 50-mil flask. Ten mils of a solution of potassium cyanid (containing 1 gm. of KCN in 500 mils of water) are then added and well shaken. An aliquot part of the filtrate, say 25 mils, is then titrated by Volhard's method with $\frac{N}{10}$ ammonium sulphocyanate for excess of silver.

Another 10 mils of silver nitrate solution is then acidified

* Romijn, Zeitschr. anal. Chem., XXXVI, 18–24 (1897).

† Bernard H. Smith, J. A. C. S., XXV, 1032 (1903).

with nitric acid and treated with 10 mils of the potassium cyanid solution to which has been added a measured quantity of dilute formaldehyde solution. The whole is made up to 50 mils and then filtered. 25 mils of the filtrate are titrated with $\frac{N}{10}$ ammonium sulphocyanate for excess of silver as before.

The difference between these two results multiplied by 2 gives the amount of potassium cyanid which was used by the formaldehyde, in terms of $\frac{N}{10}$ sulphocyanate.

Each mil of $\frac{N}{10}$ V.S. represents 0.003 gm. of formaldehyde.

The best results by this method are obtained, if the solution of formaldehyde is diluted to below 1 per cent. With 1 per cent solutions it is necessary to use 15 mils of the silver solution. In estimating very dilute solutions, it is advisable to use a 200-mil flask and to take 100 mils of the filtrate for the titration. It is possible by this method to determine with accuracy one part in 100,000.

Paraformaldehyde $(CH_2O)_3$. This is a polymeric form of formaldehyde and may be assayed by the same methods. The U.S.P. IX recommends the process in which hydrogen dioxid is used, the procedure being practically the same.

Each mil of normal alkali hydroxid V.S. corresponds to 0.03 gm. of $(CH_2O)_3$.

Acetone (Dimethyl-ketone) $(CH_3.CO.CH_3 = 58.05)$. This may be assayed by the iodometric method, used for formaldehyde. One mil of acetone is accurately weighed in a stoppered weighing-flask tared together with some distilled water. This is transferred to a 1000-mil flask and diluted to the mark with distilled water. Twenty-five mils of normal potassium hydroxid V.S. are placed in a 250-mil glass-stoppered flask and to this

is added exactly 25 mils of the acetone solution (representing one-fortieth of the weight of acetone taken), then with constant agitation of the flask, 35 mils of decinormal iodin V.S. is added, and the mixture allowed to stand for fifteen minutes. At the end of this time 26 mils of normal hydrochloric acid V.S. is added and the titration begun at once, with decinormal sodium thiosulphate V.S., using starch as indicator.

A blank test is conducted with the same quantities of reagents. The difference in the quantity of decinormal iodin V.S. consumed in the blank test and that in the assay, represents the quantity taken up by the acetone.

Each mil of this difference corresponds to 0.0009675 gm. of acetone. The reaction is

$$CH_3.CO.CH_3 + 6I + 4KOH = CHI_3 + KC_2H_3O_2 + 3KI + 3H_2O.$$

CHAPTER XVII

ESTIMATION OF ALCOHOL IN TINCTURES AND BEVERAGES

THE quantity of alcohol contained in *dilute spirit*, which leaves no residue upon evaporation, may be ascertained by taking the sp.gr. and referring to the alcohol table. When taking the specific gravity, the temperature of the liquid should be $15\frac{5}{9}°$ C. (60° F.).

In Wines, Beer, Tinctures and other alcoholic liquids containing vegetable matter, the sp.gr. of the sample is taken at $15\frac{5}{9}°$ C. (60° F.) and noted. A certain quantity (say 100 mils) is measured off and evaporated to one half, or until all odor of alcohol has passed off, the evaporation being conducted without ebullition, in order that particles of the material may not be carried off by the steam. The liquid left is then diluted with distilled water, cooled to 60° F. and made up to the original volume (100 mils), and the sp.gr. taken. Lastly, we calculate: the sp.gr. before evaporating is divided by the sp.gr. after evaporating, and the quotient will be the sp.gr. of the water and alcohol only of the liquor. Then by referring to the alcohol table the percentage of alcohol contained in the liquor is obtained.

Example. The liquor before evaporating had a sp.gr. of 0.9951; after evaporation and dilution to 100 mils the sp.gr. was found to be 1.0081.

$$\frac{.9951}{1.0081} = 0.987, \text{ the sp.gr. of the contained spirit.}$$

TABLE FOR ASCERTAINING THE PERCENTAGES RESPECTIVELY OF ALCOHOL BY WEIGHT, BY VOLUME, AND AS PROOF SPIRIT, FROM THE SPECIFIC GRAVITY.

Condensed from the excellent Alcohol Tables of Mr. Hehner in the "Analyst," vol. v. pp. 43–63.

Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me. Per cent.	Proof Spirit. Per cent.	Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me. Per cent.	Proof Spirit. Per cent.
1.0000	0.00	0.00	0.00	.9489	35.05	41.90	73.43
.9999	0.05	0.07	0.12	.9479	35.55	42.45	74.39
.9989	0.58	0.73	1.28	.9469	36.06	43.01	75.37
.9979	1.12	1.42	2.48	.9459	36.61	43.63	76.45
.9969	1.75	2.20	3.85	.9449	37.17	44.24	77.53
.9959	2.33	2.93	5.13	.9439	37.72	44.86	78.61
.9949	2.89	3.62	6.34	.9429	38.28	45.47	79.68
.9939	3.47	4.34	7.61	.9419	38.83	46.08	80.75
.9929	4.06	5.08	8.90	.9409	39.35	46.64	81.74
.9919	4.69	5.86	10.26	.9399	39.85	47.18	82.69
.9909	5.31	6.63	11.62	.9389	40.35	47.72	83.64
.9899	5.94	7.40	12.97	.9379	40.85	48.26	84.58
.9889	6.64	8.27	14.50	.9369	41.35	48.80	85.53
.9879	7.33	9.13	15.99	.9359	41.85	49.34	86.47
.9869	8.00	9.95	17.43	.9349	42.33	49.86	87.37
.9859	8.71	10.82	18.96	.9339	42.81	50.37	88.26
.9849	9.43	11.70	20.50	.9329	43.29	50.87	89.15
.9839	10.15	12.58	22.06	.9319	43.76	51.38	90.03
.9829	10.92	13.52	23.70	.9309	44.23	51.87	90.89
.9819	11.69	14.46	25.34	.9299	44.68	52.34	91.73
.9809	12.46	15.40	26.99	.9289	45.14	52.82	92.56
.9799	13.23	16.33	28.62	.9279	45.59	53.29	93.39
.9789	14.00	17.26	30.26	.9269	46.05	53.77	94.22
.9779	14.91	18.36	32.19	.9259	46.50	54.24	95.05
.9769	15.75	19.39	33.96	.9249	46.96	54.71	95.88
.9759	16.54	20.33	35.63	.9239	47.41	55.18	96.70
.9749	17.33	21.29	37.30	.9229	47.86	55.65	97.52
.9739	18.15	22.27	39.03	.9219	48.32	56.11	98.34
.9729	18.92	23.19	40.64	.9209	48.77	56.58	99.16
.9719	19.75	24.18	42.38	.9199	49.20	57.02	99.93
.9709	20.58	25.17	44.12				
.9699	21.38	26.13	45.79	.9198	49.24	57.06	100.00Ps
.9689	22.15	27.04	47.39				
.9679	22.92	27.95	48.98				
.9669	23.69	28.86	50.57	.9189	49.68	57.49	100.76
.9659	24.46	29.76	52.16	.9179	50.13	57.97	101.59
.9649	25.21	30.65	53.71	.9169	50.57	58.41	102.35
.9639	25.93	31.48	55.18	.9159	51.00	58.85	103.12
.9629	26.60	32.27	56.55	.9149	51.42	59.26	103.85
.9619	27.29	33.06	57.94	.9139	51.83	59.68	104.58
.9609	28.00	33.89	59.40	.9129	52.27	60.12	105.35
.9599	28.62	34.61	60.66	.9119	52.73	60.56	106.15
.9589	29.27	35.35	61.95	.9109	53.17	61.02	106.93
.9579	29.93	36.12	63.30	.9099	53.61	61.45	107.69
.9569	30.50	36.76	64.43	.9089	54.05	61.88	108.45
.9559	31.06	37.41	65.55	.9079	54.52	62.36	109.28
.9549	31.69	38.11	66.80	.9069	55.00	62.84	110.12
.9539	32.31	38.82	68.04	.9059	55.45	63.28	110.92
.9529	32.94	39.54	69.29	.9049	55.91	63.73	111.71
.9519	33.53	40.20	70.46	.9039	56.36	64.18	112.49
.9509	34.10	40.84	71.58	.9029	56.82	64.63	113.26
.9499	34.57	41.37	72.50	.9019	57.25	65.05	113.99

Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me. Per cent.	Proof Spirit. Per cent.	Specific Gravity 15.5°.	Absolute Alcohol by w'ght. Per cent.	Absolute Alcohol by vol'me. Per cent.	Proof Spirit. Per cent.
.9009	57.67	65.45	114.69	.8429	82.19	87.27	152.95
.8999	58.09	65.85	115.41	.8419	82.58	87.58	153.48
.8989	58.55	66.29	116.18	.8409	82.96	87.88	154.01
.8979	59.00	66.74	116.96	.8399	83.35	88.19	154.54
.8969	59.43	67.15	117.68	.8389	83.73	88.49	155.07
.8959	59.87	67.57	118.41	.8379	84.12	88.79	155.61
.8949	60.29	67.97	119.12	.8369	84.52	89.11	156.16
.8939	60.71	68.36	119.80	.8359	84.92	89.42	156.71
.8929	61.13	68.76	120.49	.8349	85.31	89.72	157.24
.8919	61.54	69.15	121.18	.8339	85.69	90.02	157.76
.8909	61.96	69.54	121.86	.8329	86.08	90.32	158.28
.8899	62.41	69.96	122.61	.8319	86.46	90.61	158.79
.8889	62.86	70.40	123.36	.8309	86.85	90.90	159.31
.8879	63.30	70.81	124.09	.8299	87.23	91.20	159.82
.8869	63.74	71.22	124.80	.8289	87.62	91.49	160.33
.8859	64.17	71.62	125.51	.8279	88.00	91.78	160.84
.8849	64.61	72.02	126.22	.8269	88.40	92.08	161.37
.8839	65.04	72.42	126.92	.8259	88.80	92.39	161.91
.8829	65.46	72.80	127.59	.8249	89.19	92.68	162.43
.8819	65.88	73.19	128.25	.8239	89.58	92.97	162.93
.8809	66.30	73.57	128.94	.8229	89.96	93.26	163.43
.8799	66.74	73.97	129.64	.8219	90.32	93.52	163.88
.8789	67.17	74.37	130.33	.8209	90.68	93.77	164.33
.8779	67.58	74.74	130.98	.8199	91.04	94.03	164.78
.8769	68.00	75.12	131.64	.8189	91.39	94.28	165.23
.8759	68.42	75.49	132.30	.8179	91.75	94.53	165.67
.8749	68.83	75.87	132.95	.8169	92.11	94.79	166.12
.8739	69.25	76.24	133.60	.8159	92.48	95.06	166.58
.8729	69.67	76.61	134.25	.8149	92.85	95.32	167.04
.8719	70.08	76.98	134.90	.8139	93.22	95.58	167.50
.8709	70.48	77.32	135.51	.8129	93.59	98.54	167.96
.8699	70.88	77.67	136.13	.8119	93.96	96.11	168.24
.8689	71.29	78.04	136.76	.8109	94.31	96.34	168.84
.8679	71.71	78.40	137.40	.8099	94.66	96.57	169.24
.8669	72.13	78.77	138.05	.8089	95.00	96.80	169.65
.8659	72.57	79.16	138.72	.8079	95.36	97.05	170.07
.8649	73.00	79.54	139.39	.8069	95.71	97.29	170.50
.8639	73.42	79.90	140.02	.8059	96.07	97.53	170.99
.8629	73.83	80.26	140.65	.8049	96.40	97.75	171.30
.8619	74.27	80.64	141.33	.8039	96.73	97.96	171.68
.8609	74.73	81.04	142.03	.8029	97.07	98.18	172.05
.8599	75.18	81.44	142.73	.8019	97.40	98.39	172.43
.8589	75.64	81.84	143.42	.8009	97.73	98.61	172.80
.8579	76.08	82.23	144.10	.7999	98.06	98.82	173.17
.8569	76.50	82.58	144.72	.7989	98.37	99.00	173.50
.8559	76.92	82.93	145.34	.7979	98.69	99.18	173.84
.8549	77.33	83.28	145.96	.7969	99.00	99.37	174.17
.8539	77.75	83.64	146.57	.7959	99.32	99.57	174.52
.8529	78.16	83.98	147.17	.7949	99.65	99.77	174.87
.8519	78.56	84.31	147.75	.7939	99.97	99.98	175.22
.8509	78.96	84.64	148.32				
.8499	79.36	84.97	148.90				
.8489	79.76	85.29	149.44		Absolute Alcohol.		
.8479	80.17	85.63	150.06				
.8469	80.58	85.97	150.67				
.8459	81.00	86.32	151.27				
.8449	81.40	86.64	151.83				
.8439	81.80	86.96	152.46	.7938	100.00	100.00	175.25

Then by referring to the table we find that this sp.gr. corresponds to 7.33 per cent, by weight, of absolute alcohol.

Another Way is to boil the liquid in a retort, condense the vapor, and when all the alcohol has passed over add sufficient water to the distillate to make up the original volume, at the temperature of 15⅝° C. (60° F.). Then, by taking the sp.gr. of this diluted distillate, the quantity of absolute alcohol is found by reference to the table. This latter method requires the taking of the sp.gr. but once and gives more accurate results.

The details of this method are as follows: Place 25 mils of the liquid measured at any definite temperature between 15° and 30° C. in a distilling flask of about 200 mils capacity and connected with a suitable condenser; add 50 mils of distilled water, distil into a 50-mil graduated flask at such a rate that about 48 mils of distillate will be received in a half hour. Dilute with water of the same temperature to 50 mils. Take the specific gravity at any definite temperature between 15° and 30° C. by means of a pycnometer, and refer to the alcoholometric table for per cent of absolute alcohol and multiply by the dilution factor to find the per cent of alcohol in the original liquid.

If the preparation is suspected to contain less than 25 per cent of alcohol, take 50 mils for analysis; if it is suspected to contain over 50 per cent, take 12.5 mils for analysis. In either case, the volume of the distillate should be made up to 50 mils.

If the preparation contains iodin, conbine it with zinc dust, or add sufficient sodium thiosulphate to take up the iodin. In the latter case add a few drops of sodium hydroxid T.S. to prevent sulphur from distilling over. If volatile acids are present, neutralize with sodium hydroxid T.S. If volatile bases are present neutralize with diluted sulphuric. If both

volatile acids and volatile bases are present, neutralize first with dilute sulphuric acid and distil about 50 mils, then neutralize the distillate with sodium hydroxid T.S. and again distil to obtain 50 mils of distillate.

If acetone, camphor, chloroform, ether, glycerin (30 per cent or over) volatile oils or other volatile products are suspected to be present, transfer the first distillate to a separator, saturate it with sodium chlorid, add 15 mils of petroleum benzin (boiling point 40–50° C.) and shake for one or two minutes. After the liquids have *completely* separated, draw off the lower alcoholic salt solution into a second separator and repeat the extraction with 15 mils of petroleum benzin. Again draw of the lower alcoholic salt solution. Introduce this into a 200-mil distilling flask. Wash the combined benzin solutions with about 25 mils of saturated sodium chlorid solution and add the washings to the distilling flask, and distil about 45 or 48 mils, bring to the original temperature, dilute with water of the same temperature to 50 mils, determine specific gravity and alcohol per cent as directed above.

PART III

A FEW GASOMETRIC ANALYSES

CHAPTER XVIII

THE NITROMETER

For general gas analysis, and for the rapid estimation of such substances as ethyl nitrite, hydrogen dioxid, urea, bleaching powder, manganese dioxid, etc., an instrument called the *nitrometer* is used.

The apparatus in its simplest form is shown in Fig. 57. It consists of a measuring tube, *a*, of 50- or 100-mils capacity, and graduated in tenths of a mil. This is connected by means of a stout rubber tube with an open equilibrium tube, *b*, also called "control-tube," "pressure-tube," or "level-tube." Both tubes are preferably provided with a globular expansion near the lower end, and are held by suitable clamps upon a stand, in such a manner that either tube may be readily and quickly clamped at a higher or lower level. The measuring tube is fitted at the top with a stop-cock, *c*, and a graduated glass tube or cup, *d*. Some nitrometers are provided with a three-way stop-cock, so arranged that according to the way it is turned, it will discharge the contents of the cup either into the measuring tube below, or out into the

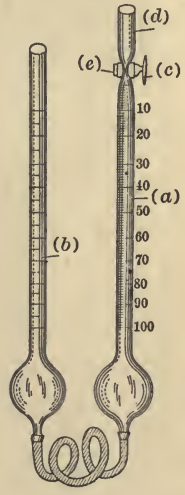

Fig. 57.

waste opening which is usually placed at *e*, or it will discharge the contents of the measuring tube into the waste opening.

With this apparatus gases can be rapidly and accurately measured at definite temperature and pressure.

In measuring the gas the instrument is filled with some liquid in which the gas is insoluble—generally mercury. In many cases a saturated solution or salt may be used.

Suppose we fill the instrument with mercury in such quantity that when the stop-cock is opened and the control-tube raised, the mercury will rise as far as the top, and about two inches in the control-tube.

The top is now closed, the control-tube lowered, and a little carbonic acid gas admitted through *e*. The top is then again closed, and the instrument allowed to stand until its contents have acquired the temperature of the room. A centigrade thermometer suspended to the stand will then give the temperature of the gas.

The control-tube is now raised or lowered so as to make the level of the liquid in both tubes the same. This makes the pressure in the tube the same as the atmospheric pressure outside, and, by referring to a barometer standing near, this pressure is ascertained.

We now have a definite volume of the gas at a known temperature and pressure.

It now only remains to read off the volume of the gas, and correct it to the normal temperature and pressure by Charles' and Boyle's laws, respectively.

The normal temperature and pressure is 0° C. and 760 mm. pressure. Although the U.S.P. adopts a standard temperature of 25° C.

The weight of the gas in grams may then be calculated from its volume by multiplying the number of mils at the normal temperature and pressure, by the weight of 1 mil of the gas in grams.

This weight may be found as follows:

1000 mils of hydrogen at normal temperature and pressure weigh 0.0896 gm. One mil of H then weighs 0.0000896 gm.

One mil of oxygen weighs sixteen times as much, and 1 mil of nitrogen weighs fourteen times as much. Therefore, by multiplying the weight of 1 mil of H by the atomic weight of an elementary gas, or half the molecular weight of a compound gas, the weight of 1 mil of that gas is obtained.

According to the Law of Charles, *the volume of a gas under constant pressure varies directly with the absolute temperature.*

All gases expand or contract by $\frac{1}{273}$ of their volume for each centigrade degree of temperature increased or decreased.

We may regard a gas at 0° C. as having passed through 273° C. In other words, 273° below zero must be regarded as the absolute zero, and 0° C. as 273° absolute temperature.

Thus the absolute temperature centigrade is the observed temperature + 273°.

Example. A given volume of oxygen gas at 15° C. measures 20 mils. What will it measure at 0° C.?

$$\frac{0^\circ + 273^\circ \times 20}{15^\circ + 273^\circ} \quad \text{or} \quad \frac{273^\circ \times 20}{288^\circ} = 18.95 \text{ mils.} \quad \textit{Ans.}$$

Boyle's Law. The volume of a confined gas is inversely proportional to the pressure brought to bear upon it. That is, the less the pressure, the greater the volume, and *vice versa.*

Rule. Multiply the observed volume by the observed pressure, and divide by the normal pressure.

Example. A given volume of gas at 750 mm. pressure

measures 20 mils. What will it measure at 760 mm. (the normal pressure)?

$$\frac{750 \times 20 \text{ mils}}{760} = 19.73 \text{ mils.} \quad \textit{Ans.}$$

Now let us take an example in which both laws are involved.

A given volume of oxygen at 15° C. subjected to a pressure of 750 mm. measures 20 mils. What will it measure at the normal temperature and pressure?—i.e., 0° C. and 760 mm.

In the first example we find that 20 mils of oxygen at 15° C. will measure at 0° C. 18.95 mils. Then

$$\frac{750 \times 18.95 \text{ mils}}{760} = 18.70 \text{ mils.} \quad \textit{Ans.}$$

Now to find the weight of this volume of oxygen, we proceed as follows:

1 mil of H weighs 0.0000896 gm.;
1 mil of O weighs $16 \times 0.0000896 = 0.0014336$ gm.;
18.70 mils of O = 18.70×0.0014336 gm., or 0.02680832 gm.

In the U.S.P. the standard for temperature and pressure is 25° C. and 760 mm. and hence all pharmaceutical assays should be made in accordance with this standard, and all gases measured at this temperature and pressure, or corrections made by calculation.

Example. A volume of gas measures 20 mils at 15° C. What will it measure at 25° C.?

$$\frac{25^\circ + 273^\circ \times 20}{15^\circ + 273^\circ} \quad \text{or} \quad \frac{298 \times 20}{288} = 20.7 \text{ mils.}$$

The following tables from the United States Pharmacopœia IX will be found very useful for making temperature and pressure corrections.

FACTORS FOR TEMPERATURE CORRECTIONS

(Normal Temperature, 25° C.)

Temperature.	Factor.	Temperature.	Factor.	Temperature.	Factor.
15° C.	1.035	22° C.	1.010	29° C.	0.987
16° C.	1.031	23° C.	1.007	30° C.	0.983
17° C.	1.028	24° C.	1.003	31° C.	0.980
18° C.	1.024	25° C.	1.000	32° C.	0.977
19° C.	1.021	26° C.	0.997	33° C.	0.974
20° C.	1.017	27° C.	0.993	34° C.	0.971
21° C.	1.014	28° C.	0.990	35° C.	0.968

Example. Assuming that the volume of a gas read off was 41 mils at 30° C. and it is desired to ascertain the corresponding volume at 25° C., then the 41 mils must be multiplied by 0.983. The result will be 40.30 mils as the equivalent volume of gas at 25° C.

FACTORS FOR CORRECTION FOR BAROMETRIC PRESSURE

(Normal Barometer, 760 mm.)

Barometer Reading.		Factor.	Barometer Reading.		Factor.
Millimeters.	Inches.		Millimeters.	Inches.	
790	31.10	1.039	660	25.98	0.868
780	30.71	1.026	650	25.59	0.855
770	30.31	1.013	640	25.20	0.842
760	29.92	1.000	630	24.80	0.829
750	29.53	0.987	620	24.41	0.816
740	29.13	0.974	610	24.02	0.803
730	28.74	0.961	600	23.62	0.789
720	28.35	0.947	590	23.23	0.776
710	27.95	0.934	580	22.83	0.763
700	27.56	0.921	570	22.44	0.750
690	27.17	0.908	560	22.05	0.737
680	26.77	0.895	550	21.65	0.724
670	26.38	0.882	540	21.26	0.711

Example. Assuming that the volume of gas read off was 41 mils at 590 mm. barometric pressure, and it is desired to ascertain the corresponding volume at normal pressure (760 mm.), then the 41 mils must be multiplied by 0.776. The result will be 31.81 mils.

CHAPTER XIX

ASSAY OF NITRITES

Spirit of Nitrous Ether. This is an alcoholic solution of ethyl nitrite ($C_2H_5NO_2 = 75.05$), yielding, when freshly prepared and tested in the nitrometer, not less than 11 times its own volume of nitrogen dioxid ($NO = 30.01$).

When nitrites are mixed with an excess of KI and acidulated with H_2SO_4, iodin is liberated, and all the nitrogen of the nitrite is evolved in the form of NO, as shown in the equation

$$\underset{150.1}{2C_2H_5NO_2} + 2KI + 2H_2SO_4 = 2C_2H_5OH + 2KHSO_4 + I_2 + \underset{60.02}{2NO}.$$

The process is conducted as follows:

Open the stop-cock of the measuring tube, raise the control-tube, and pour into the latter a saturated solution of NaCl until the measuring tube, including the bore of the stop-cock, is completely filled. Then close the stop-cock and fix the control-tube at a lower level. Now introduce into the funnel at the top of the measuring tube a weighed quantity (about 4 gms.) * of spirit of nitrous ether; open the stop-cock and allow the spirit to run into the nitrometer, being careful that

* It is conveninent to take 5 mils accurately measured, and calculate its weight by multiplying by the specific gravity, but better to take about 40 mils of the spirit, weigh it accurately, and then add sufficient alcohol to make exactly 100 mils. This is mixed thoroughly and 10 mils of the solution taken for analysis.

no air enters at the same time. Ten mils of potassium iodid T.S. are now added in the same manner, and followed by 10 mils of normal sulphuric acid V.S. Effervescence takes place immediately, and after thirty to sixty minutes, when the volume of gas has become constant, the control-tube is lowered so as to make the level of the liquid in both tubes the same, and the volume of the gas in the graduated tube read off.

This volume, multiplied by 0.00307 gm., gives the weight of ethyl nitrite in the spirit taken for analysis. The product multiplied by 100, and then divided by the weight of the spirit taken, gives the per cent of pure ethyl nitrite present.

The temperature correction is one-third of one per cent of the total percentage found, for each degree, additive if the temperature is below, subtractive if above 25° C. The barometric correction is $\frac{3}{40}$ of one per cent for each millimeter, additive if above, subtractive if below, 760.

The volume of NO generated at the ordinary indoor temperature (assumed to be at or near 25° C., 77° F.) should not be less than 55 mils if 5 mils of the spirit are taken, corresponding to about 4 per cent of pure ethyl nitrite.

Sodium chlorid solution is used in the above assay, because, owing to its density, the spirit will float on top, and the gas evolved will not dissolve in it. At the same time the expense of using mercury is saved. It is important that no air be allowed to get into the measuring tube, because this would convert the NO into a higher oxid of nitrogen, which would dissolve in the salt solution, and thus vitiate the result.

Example. Four gms. of spirit of nitrous ether (sp.gr. 0.823) are treated in a nitrometer, and the NO evolved measures 55 mils.

The temperature at which the operation is conducted is 25° C., and the atmospheric pressure normal.

What per cent of ethyl nitrite is present in the sample?

$$\frac{0.00307 \times 55 \times 100}{4} = 3.72 \text{ per cent.}$$

Amyl Nitrite is a liquid containing about 80 per cent of amyl nitrite (principally iso-amyl nitrite), $C_5H_{11}NO_2 = 117.09$, together with variable quantities of undetermined compounds.

The assay is as follows: Take about 3 mils of the amyl nitrite, which has been previously shaken with 0.5 gm. of potassium bicarbonate and carefully decanted. Put into a tared 100-mil measuring flask, and weigh it accurately; add alcohol to bring the volume to exactly 100 mils. Ten mils of this alcoholic solution are introduced into the nitrometer as directed for spirit of nitrous ether; 10 mils of potassium iodid solution (20 per cent) and 10 mils of $\frac{N}{1}$ H_2SO_4 V.S. are then added, and the volume of NO generated, measured at the ordinary indoor temperature (25° C. or 77° F.), should be about 40 mils. Each mil at this temperature represents 0.0048 gm. of pure amyl nitrite.

Sodium Nitrite ($NaNO_2 = 69.01$). This, like the other nitrites mentioned, when treated with potassium iodid and sulphuric acid, is decomposed, and NO is given off. The reaction is here illustrated:

$$2NaNO_2 + 2KI + 2H_2SO_4 = K_2SO_4 + Na_2SO_4 + 2H_2O + 2NO + I_2.$$

A molecule of $NaNO_2$ (69.01) evolves, when properly treated, one molecule of NO (30.01).

The assay process is as follows: Weigh out 0.15 gm. of $NaNO_2$, dissolve it in about 5 mils of water, and introduce the solution into a nitrometer. This is followed by a solution

of 1 gm. of KI in 6 mils of water and 15 mils of $\frac{N}{1}$ H_2SO_4. The gas which is liberated should measure not less than 50 mils at 15° C. (59° F.) or 51.7 mils at 25° C. (77° F.), corresponding to not less than 97.6 per cent of the pure salt. Each mil at 25° C. represents 0.002837 gm. and at 0° C. 0.0030916 gm. of pure $NaNO_2$.

Nitric Acid in Nitrates. This may also be effected by the use of the nitrometer.

When a nitrate is shaken up with an excess of sulphuric acid and mercury, the nitrate is decomposed and NO is evolved, as seen in the following equation:

$$\underset{2)202.22}{2KNO_3} + 4H_2SO_4 + 3Hg = 3HgSO_4 + K_2SO_4 + \underset{2)60.02}{2NO} + 4H_2O.$$
$$\underline{\quad 101.11 \quad} \qquad\qquad \underline{\quad 30.01 \quad}$$

Thus each molecule of the nitrate radical NO_3 gives off a molecule of NO.

Not more than 0.2 gm. of nitrate should be taken for analysis, since, if this quantity is exceeded, the volume of gas evolved willl be greater than the instrument can conveniently hold. In this estimation the nitrometer is filled with mercury instead of brine; the nitrate is dissolved in 5 cc. of water, introduced into the nitrometer, and followed by excess of strong sulphuric acid. The instrument is well shaken for some time, and when action has ceased and the contents have cooled down to the temperature of the room, the level is adjusted and the volume of NO read off and calculated in the usual way.

ESTIMATION OF NITROGEN DIOXID

$NO = 30.01$; 1 liter at 0° C. and 760 mm. = 1.3406 gms.
at 25° C. and 760 mm. = 1.2281 gms.

ONE MILLILITER OF NITROGEN DIOXID IS THE EQUIVALENT OF:

	At 0° C. and 760 mm. Gram.	At 25° C. and 760 mm. Gram.
Nitrogen dioxid, $NO = 30.01$	0.0013406	0.0012281
Amyl nitrite, $C_5H_{11}NO_2 = 117.10$	0.005231	0.0048
Ethyl nitrite, $C_2H_5NO_2 = 75.05$	0.0033528	0.003071
Sodium nitrite, $NaNO_2 = 69.01$	0.0030828	0.002824

CHAPTER XX

HYDROGEN DIOXID

As stated in a previous chapter, hydrogen dioxid when acted upon by an acidulated solution of potassium permanganate, is decomposed and oxygen is evolved. One-half of this oxygen comes from the dioxid and the other half from the permanganate.

Therefore if 1 mil of the dioxid be treated in this way and 20 mils of oxygen are evolved, the strength of the solution is 10 volumes.

The nitrometer may be used for this estimation.

This instrument is charged with a concentrated solution of sodium sulphate (which in this case is better than brine), and 1 mil of the dioxid introduced from the funnel, followed by excess of solution of permanganate acidulated with sulphuric acid.

This latter solution should be of such strength that when the reaction is completed, the solution should still have a purple color.

The reaction is thus illustrated:

$$5H_2O_2 + 3H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

By the use of *Squibb's Urea Apparatus* (Fig. 61) the estimation may be easily and rapidly made.

Into the generating bottle is put about 30 mils of a strong, acidulated solution of potassium permanganate, and a small test-tube containing 1 mil of H_2O_2 is carefully introduced. The two liquids must not be allowed to come in contact.

The larger flask is filled with water, or better, a solution of sodium sulphate; the connection is then made by means of the rubber tube, and the generating-bottle tipped over and agitated so that the liquids will mix and the reaction take place.

The liberated oxygen then passes into the larger bottle, displacing an equal volume of water, which is collected and measured. Half of this volume represents the volume strength of the H_2O_2.

An Improvised Nitrometer may be used. The author has found the following instrument convenient:

To the bottom of an ordinary 50-mil burette is attached a suitable length of rubber tubing, to the other end of which is attached another burette or *ungraduated* tube, which serves as a control-tube.

Into the top of the burette is fitted a rubber stopper, through which passes a short glass tube, which is connected by means of a rubber tube to a generating-bottle similar to that used with *Squibb's Urea Apparatus*. Into the control-tube is poured the solution of sodium sulphate, sufficient to fill the burette to the zero mark and have the surface of the liquid in both tubes on a level.

About 30 mils of strong permanganate solution acidulated with sulphuric acid are now placed in the generating-bottle, and then the small test-tube or homeopathic vial, containing exactly 1 mil of hydrogen dioxid, is placed in. The generating bottle is then stoppered and agitated, the evolved gas passes over, and forces down the liquid in the burette; the control-tube is then lowered so as to bring the surfaces of the liquid in both tubes on a level.

The reading is then taken.

Each mil of gas represents one-half volume of oxygen evolved from the dioxid if 1 mil of the latter is used. Each mil

of oxygen evolved from 1 mil of the dioxid represents also 0.0017 gm. of absolute H_2O_2, or 0.0008 gm. of available oxygen.

Thus if from 1 mil of the solution of hydrogen dioxid 20 mils of gas are evolved, it is a so-called ten-volume solution and contains $0.0017 \times 20 = 0.034$ gm. of absolute H_2O_2, or $0.0008 \times 20 = 0.016$ gm. of available oxygen.

According to Naylor and Dyer (Trans. Brit. Ph. Conf., 1901, 339) the gasometric permanganate method is unreliable, because under the conditions of the test sulphuric acid added to the brine solution in the nitrometer naturally liberates a little hydrochloric acid, and this in the presence of permanganate becomes to some extent decomposed into chlorin. It is the uncertainty as to the extent to which the chlorin is absorbed by the water, which renders the accuracy of the method doubtful. The results of this method are uniformly too high, whether the gas be collected over mercury, over saturated magnesium sulphate, or over brine, and in the latter case considerably higher. But when the dichromate V.S. is used (without acid), closely concordant results are obtained, whether the gas be collected over mercury, or the other solutions. The evolution of oxygen by the latter method is slower than when permanganate is used, but the oxygen obtained represents the volume available in the sample.

In the **Hypochlorite Method,** the nitrometer is filled with a saturated solution of sodium chlorid. Two mils of the hydrogen dioxid are admitted into the measuring tube, the funnel tube filled with a little water, and this also let in, then 20 mils of the chlorinated lime solution introduced. From this point the procedure is the same as in the gasometric permanganate method.

$$Ca(ClO)_2 + 2H_2O_2 = O_4 + CaCl_2 + 2H_2O.$$

The presence of preservatives, except inorganic ones, gives low results.

The Hypobromite Method. W. M. Dehn (J. A. C. S., XXIX (9), 1315) describes an accurate and rapid determination of hydrogen dioxid by means of sodium hypobromite, using a ureometer. The reaction involved is

$$H_2O_2 + NaBrO = NaBr + H_2O + O_2.$$

The apparatus is shown in Fig. 58. The following description of the method is by Dehn from the Journal of the American Chemical Society.

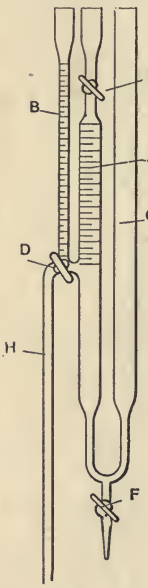

FIG. 58.

"The stop-cock *E* is opened and the stop-cocks *D* and *F* are closed; then the solution of sodium hypobromite * is poured in at the top of *C* until it fills the tubes *A* and *C* to some point above the stop-cock *E*.

"The stop-cock *E* is then closed and the stop-cock *F* is opened, so that the hypobromite in *C* may run down to the constricted portion; the solution in *A* is then sustained by atmospheric pressure. The stop-cock *D* (arranged so as to deliver only in the two directions of a right-angle triangle) is turned from the position shown in the figure and is so controlled that *B* may first be washed with a little of the hydrogen peroxid and then be filled with the same to a readable height on the scale. Upon turning *D* so as to admit a regulated volume of the hydrogen peroxid solution an immediate evaluation of oxygen results. After admitting most of the hypobromite held above *E*, and letting stand for a minute or two so as to drain properly, the columns of hypobromite in *A*

* This solution is prepared as directed under Estimation of Urea, except that it is finally diluted with an equal volume of water.

and *C* are brought to the same level, the volume of oxygen is read off and its weight and that of the corresponding hydrogen dioxid are calculated by the usual formulas."

The author of this method also gives the following table, by means of which the mils of oxygen, under various conditions of temperature and pressure, may be calculated into milligrams of hydrogen dioxid, and claims that by the use of this instrument, this hypobromite method and the table for calculating the assay of hydrogen dioxid, is not only rapid and accurate, but the necessity of preparing and correcting standard solutions is avoided and the presence of the usual preservatives used in the dioxid solution may be ignored.

WEIGHT IN MILLIGRAMS OF H_2O_2 CORRESPONDING TO ONE CUBIC CENTIMETER OF MOIST OXYGEN

t/mm.	728	732	736	740	744	748
4°	1.2664	1.2734	1.2802	1.2872	1.2942	1.3011
8	1.2463	1.2531	1.2600	1.2669	1.2736	1.2805
12	1.2251	1.2317	1.2387	1.2454	1.2522	1.2589
16	1.2044	1.2111	1.2178	1.2245	1.2311	1.2378
20	1.1817	1.1884	1.1948	1.2015	1.2080	1.2145
24	1.1583	1.1649	1.1719	1.1777	1.1843	1.1907
28	1.1345	1.1411	1.1476	1.1538	1.1603	1.1665
32	1.1085	1.1149	1.1213	1.1275	1.1338	1.1401
36	1.0843	1.0905	1.0967	1.1030	1.1093	1.1155
40	1.0605	1.0666	1.0725	1.0786	1.0849	1.0909

t/mm.	752	756	760	764	768
4°	1.3081	1.3151	1.3222	1.3290	1.3359
8	1.2876	1.2944	1.3014	1.3081	1.3150
12	1.2657	1.2726	1.2823	1.2860	1.2928
16	1.2444	1.2512	1.2578	1.2946	1.2713
20	1.2213	1.2279	1.2345	1.2410	1.2475
24	1.1972	1.2036	1.2100	1.2169	1.2230
28	1.1731	1.1796	1.1857	1.1922	1.1986
32	1.1465	1.1528	1.1589	1.1562	1.1715
36	1.1214	1.1279	1.1341	1.1402	1.1465
40	1.0971	1.1033	1.1094	1.1155	1.1216

CHAPTER XXI

ESTIMATION OF SOLUBLE CARBONATES BY THE USE OF THE NITROMETER

THE nitrometer may be used for estimating ammonium carbonate in **aromatic spirit of ammonia.**

The nitrometer in this case must be charged with mercury, as the liberated CO_2 is soluble in aqueous liquids.

A given volume of the spirit is introduced into the nitrometer followed by an excess of dilute HCl, and the evolved gas then read off; and from its quantity the proportion of ammonium carbonate may be calculated by applying the equation

$$\underset{*96}{(NH_4)_2CO_3} + 2HCl = 2NH_4Cl + H_2O + \underset{*44}{CO_2}.$$

The volume of gas liberated must first be reduced to its corresponding volume at 0° C.

Each mil of CO_2 at 0° C. weighs 0.001966 gm. Now if 44 gms. of CO_2 represent 96 gms. of normal ammonium carbonate, how much ammonium carbonate does 0.001966 gm. of CO_2 represent?

$$44 : 96 :: 0.001966 : x. \qquad x = 0.004289 \text{ gm.}$$

Thus each mil of CO_2 at normal pressure and 0° C. represents 0.004289 gm. of $(NH_4)_2CO_3$, approximately.

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* The atomic weights are approximate.

CHAPTER XXII

ESTIMATION OF UREA IN URINE

THE determination of urea is based upon the fact that when urea is decomposed by an alkaline hypochlorite or hypobromite, carbon dioxid and nitrogen are given off, as the equation shows:

$$CO(NH_2)_2 + 3NaBrO = 3NaBr + CO_2 + N_2 + 2H_2O.$$

The liberated N may be measured, and from its quantity the amount of urea calculated. The other products of the decomposition go into solution.

The hypobromite solution is prepared as follows: 100 gms. NaOH are dissolved in 250 mils of water, and when this solution has become cold 25 mils of bromin are added, and the solution kept cold. This solution contains sodium hypobromite, bromate and hydroxid. It readily undergoes decomposition, and should therefore always be freshly prepared when wanted for use. To 15 mils of the NaOH solution add 1 mil of bromin.

The solution of sodium hypochlorite is generally preferred to the hypobromite, because it is more stable, just as efficacious, and the disagreeable handling of bromin is obviated.

Various forms of apparatus have been devised for the quantitative estimation of urea.

The Doremus Ureometer (Fig. 59) is the simplest of these. The long arm of the *ureometer* is filled with the hypobromite solution, and then 1 mil of the urine is introduced by the aid of the pipette. The pipette is introduced through the bulb

as far as it will go in the bend, and the nipple is then gently but steadily compressed, being careful that no air is admitted.

The volume of the liberated gas is read off after the froth has subsided.

The ureometer indicates, according to its graduation, either milligrams of urea in 1 mil or grains of urea per fluid ounce of urine.

It also indicates by the signs +, N, and − whether the

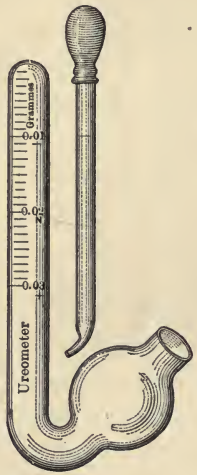

Fig. 59.

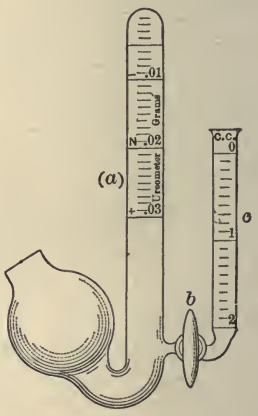

Fig. 60.

urea is present in an increased, normal or decreased quantity.

Either Knop's or Squibb's solution, or Liquor Sodæ Chloratæ U. S. P. may be used in this instrument. Knop's solution is that described above. Squibb's solution contains potassium bromid as well as bromin. It is prepared by taking an equal weight of bromin and of potassium bromid, and adding eight times as many cc. of water as there were grams of bromin taken. For use mix equal volumes of this solution with the sodium hydroxid solution above described.

The Hinds-Doremus Ureometer. This apparatus, which is shown in Fig. 60, is capable of giving more exact results than the original apparatus, because the 1 mil of urine can be delivered more accurately. It consists of a bulb with an upright tube *a*, graduated like the original, so that each of the smallest divisions represents 0.001 gm. of urea in the urine used. The lower portion of this tube is, in connection with a smaller tube *c*, graduated with a capacity of 2 mils; between these tubes a glass stop-cock is situated. Closing the stop-cock *b*, Knop's or Squibb's fluid (diluted one half) or liquor sodæ chloratæ U. S. P. is introduced into tube *a* so as to

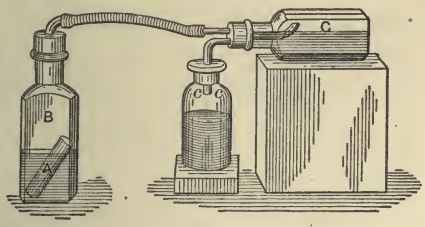

Fig. 61.

completely fill it. The apparatus is then placed in an upright position and the smaller tube *c* is filled to the zero mark with urine. The stop-cock is then turned slowly so as to admit gradually 1 mil of the urine to tube *a*. After fifteen minutes the reading is taken. If the reading be 0.015 and the amount of urine taken was 1 mil, then multiplying by 100 gives 1.5 per cent of urea.

Squibb's Urea Apparatus (Fig. 61) is a very simple apparatus, and can be easily improvised in a drug store. It consists of two wide-mouthed bottles, the larger of which, *C*, capable of holding about 250 mils, is fitted with a rubber stopper, through which is passed a curved delivery tube and a short straight tube, the latter connected by a piece of rubber tubing

to the short glass tube in the rubber stopper of the smaller or generating-bottle *B*. In the generating-bottle is a small test-tube *A*.

Into the test-tube *A* is placed 5 mils of urine, and into the smaller bottle *B* is put 20 mils of the hypobromite solution, or strong liquor sodæ chloratæ. The test-tube is then placed in the generating-bottle *B*, being careful that the urine and the reagent do not come in contact. The larger bottle *C* is now filled with water and the two bottles connected by the rubber tube, the larger bottle being placed on its side upon a block, and when all connections are tight, the generating-bottle is shaken so that the urine will mix with the reagent.

Decomposition takes place, and the generated gas passes into the bottle *C*, displacing water, which is caught in a graduated cylinder or other measuring vessel. The volume of water displaced is equivalent to the volume of gas evolved.

Each mil of nitrogen gas evolved at 0° C. and normal pressure represents 0.00268 gm. of urea. Then by multiplying the number of mils evolved by this number the quantity of urea in the 5 mils of urine taken is ascertained.

The volume of gas obtained when the operation is conducted at ordinary temperatures should always be reduced to its corresponding volume at 0° C. and 760 mm.

The factor 0.00268 is found in the following manner:

1000 mils of H at 0° C. weigh 0.0896 gm.;
1000 mils of N at 0° C. weigh 1.255 gms.

By the equation it is seen that 60.02 gms. of urea evolve when decomposed 28.02 gms. of N.

$$\underset{60.02}{CO(NH_2)_2} + 3NaBrO = 3NaBr + CO_2 + \underset{28.02}{N_2} + 2H_2O.$$

Now we will find the volume occupied by 28.02 gms. of N at 0° C.

1.255 gms. of N = 1000 mils.

gms. mils gms. mils

1.255 : 1000 :: 28.02 : x. $x = 22326$.

Thus 60.02 gms. of urea evolve 22326 mils of N. One mil of N thus represents 0.00268 gm. of urea.

APPENDIX

DESCRIPTION OF INDICATORS

THE following list includes the more reliable indicators in common use, arranged alphabetically.

Alizarin: alkalies = *Red*; acids = *Yellow*

This dye was first found in the roots of madder (*Rubia tinctorium*) but is now also obtained synthetically. A half per cent solution in alcohol is employed as an indicator.

Azolitmin: alkalies = *Blue*; acids = *Red*

This is the color principle to which litmus owes its value as an indicator. Its extraction is explained under litmus. It is a high-priced article and is in consequence seldom used, the purified litmus tincture being preferred.

Brazil Wood Solution: alkalies = *Purplish-red*; acids = *Yellow*

Boil 50 gms. of finely-cut Brazil-wood (the heart-wood of *Peltophorum dubium* (Sprengel) Briton, nat. ord. *Leguminosæ*) with 250 mils of water during half an hour, replacing from time to time. Allow the mixture to cool; strain; wash the contents of the strainer with water until 100 mils of strained liquid are obtained; add 25 mils of alcohol and filter.

This indicator is especially serviceable for the titration of

alkaloids, but it is useless in the presence of sulphurous acid, sulphites, or sulphids, as these substances decolorize the solution.

Cochineal: alkalies = *Violet*
acids = *Yellowish-red*

Cochineal is the dried female insect, *Pseudococcus cacti* Linné.

The test solution is made by macerating 3 gms. of unbroken cochineal for four days in 250 mils of a mixture of 1 part of alcohol and 3 parts of water, by volume. It should be neutralized with ammonia water before using.

It is a very valuable indicator, especially for carbonates of the alkalies and alkaline earths, because it is not affected by CO_2. It is also useful for titrating alkaloids, alkalies, alkali earths, ammonia, and inorganic acids, but is useless for most organic acids.

Congo Red: alkalies = *Red*
acids = *Blue*

Congo red is a sodium tetrazo-diphenyl-naphtionate. It occurs in commerce in the form of lumps of a reddish-brown color. It is readily soluble in both water and alcohol. Its solution is exceedingly sensitive to free acids even in the presence of acid salts, and is likewise very sensitive to free carbonic and acetic acids. It may be employed for estimating free mineral acids, in the presence of most organic acids.

The test solution contains 1 per cent of the dye and 10 per cent of alcohol.

Gallein: alkalies = *Bright red*
acids = *Pale brown*

Anthracene violet or pyrogallol-phthalein was proposed by M. Dechan for use as an indicator.

It is prepared by heating a mixture of one part of phthalic

anhydrid and two parts of pyrogallol, and finally recrystallizing in a similar way to phenolphthalein.

It is described as a dark reddish crystalline solid, possessing a greenish luster. It is nearly insoluble in water, but readily soluble in alcohol. In commerce it is frequently found as a paste, mixed with water.

It forms a red coloration with alkalies, which is changed to yellowish-brown on addition to an acid in excess.

It is said to be more delicate toward alkalies than phenolphthalein, and may be used in its stead for titrating many of the alkaloids. It may be used in the presence of ammonia or its salts. It indicates sharply with the organic acids. A solution in rectified spirit 1–1000 is generally employed.

Hæmatoxylin: alkalies = *Violet*
acids = *Yellow to orange*

A peculiar principle obtained from logwood, having the composition $C_{16}H_{14}O_6$, and crystallizing with one or three molecules of water. It is an efflorescent yellowish-rose colored substance, but when pure is said to be colorless, reddening on exposure to light.

It is soluble in hot water or alcohol. Its alcoholic solution is largely used as an indicator in the titration of alkaloids, for which it is considered the indicator par excellence.

The solution is prepared by dissolving 0.3 gm. of the well-crystallized material in 100 mils of alcohol. In titrating use about three drops of this solution.

Its color reaction with carbonates and bicarbonates is interesting. When added to a solution of alkali-bicarbonate the reaction requires many seconds, and results in a gradually deepening carmine-red which is permanent, while in the case of soluble carbonates the reaction is instantaneous, a purple-red which changes rapidly through cherry, eosin-red to orange.

The reaction with ammonium carbonate is similar to that with bicarbonate.

Iodeosin: alkalies = *Rose-red*
acids = *Yellow*

Tetra-iodo-fluorescein Erythrosin B. This indicator is useful for minute quantities of alkali, as for instance, such as may be dissolved out from glass on contact with water. It is used in connection with highly dilute standard solutions only. The iodeosin solution is made by dissolving 0.002 gm. of the indicator in 1000 mils of pure ether. Titration with this indicator is carried out by introducing 50 to 100 mils of the liquid to be titrated into a stoppered bottle and adding 10 to 20 mils of the ethereal indicator solution and setting aside after shaking. The ethereal layer as well as the fluid will be colorless if the latter is neutral, but if traces of alkali are present the rose-red tint passes into the aqueous liquid leaving the ether colorless. If the fluid is acid, the ethereal layer is yellow. If preferred, 4 or 5 drops of a 1–10,000 alcoholic solution of the indicator may be added to the liquid, and ether then added. Iodeosin is particularly useful in titration of alkaloids, especially those of weak basicity, as emetine, atropine, morphine, etc.

Lacmoid: alkalies = *Blue*
acids = *Red*

Lacmoid is somewhat allied to litmus, but differs from it in many respects. It is a product of resorcin, and may be prepared by heating gradually to 110° C. a mixture of 100 parts of resorcin, 5 parts of sodium nitrite, and 5 parts of water. After the violent reaction moderates it is heated to 120° C. until ammonia ceases to be evolved. The residue is then dissolved in warm water and the lacmoid precipitated therefrom by HCl; the free acid is then removed by washing and the residue dried.

This constitutes the commercial lacmoid, which is not in a sufficiently pure state to be used as an indicator; its purification is effected according to Förster by treating the powder with boiling water and acidulating the resulting blue solution with hydrochloric acid. After a few hours the precipitate is collected and washed with a little cold water and carefully dried, or it is dissolved in alcohol and the solution evaporated. Even after careful purification, lacmoid solution may still exhibit a violet tinge, which is a disturbing factor in accurate work. To remedy this defect, Förster suggests the addition of 5 gms. of beta-naphthol green to 3 gms. of purified lacmoid dissolved in 700 mils of water and 300 mils of alcohol. A sample of lacmoid which is only sparingly soluble in water should be rejected. The purer the article the more readily does it dissolve in water. A good T.S. may be made by dissolving 1 part in 12 parts of 20 per cent alcohol, filtering and evaporating in vacuo over sulphuric acid. Of the residue obtained in this way 0.2 gm. is dissolved in 100 mils of alcohol.

Lacmoid paper is prepared by dipping slips of calendered unsized paper into the blue or red solution and drying them.

Lacmoid is slightly affected by carbonic-acid gas. It may be used cold for the alkaline and earthy hydroxids, arsenites, and borates and the mineral acids. The carbonates and bicarbonates of the alkalies and alkali earths are titrated hot with this indicator.

Many of the metallic salts, such as the sulphates and chlorids of iron, copper and zinc, which are more or less acid to litmus, are neutral to lacmoid; therefore free acids in such solutions may be estimated by its aid.

Lacmoid paper reacts alkaline with the chromates of potassium or sodium, but neutral with the dichromates, so that a mixture of the two or of chromic acid and dichromate may be titrated by its aid.

Litmus (*Lacmus*): alkalies = *Blue*, acids = *Red*

A pigment obtained by the fermentation of certain lichens, principally from *Roccella tinctoria* and *R. fuciformis*, but also from other species of lichen.

It occurs in commerce in small, friable, light cakes or cubes, of a violet color.

The coloring principles of litmus are azolitmin, erythrolitmin, and erythrolein. The first, which is the most important, is soluble in water, but insoluble in alcohol. The other two are readily soluble in alcohol, but only sparingly soluble in water.

The process for making litmus test solution consists in exhausting coarsely powdered litmus with boiling alcohol.

The residue is then digested with about an equal weight of cold water so as to dissolve the excess of alkali present.

The blue solution thus obtained, after being acidulated, may be used to make *red litmus-paper*. Finally, the residue is extracted with about five times its weight of boiling water and the solution filtered.

The filtrate is preserved as *test solution* in wide-mouthed bottles, stoppered with loose plugs of cotton to exclude dust, but to admit air.

When kept in closed vessels litmus solution gradually loses color, but this returns upon exposure to air and consequent absorption of oxygen.

The fermentation to which the loss of color is due may be prevented by saturating the solution with NaCl or by the addition of thymol or phenol.

The British Pharmacopœia recommends the boiling of litmus in powder with three succcessive portions of rectified spirit, and then to digest the residue in distilled water and filter, the object of these steps in the process being to get rid of

the greater portion of erythrolitmin and erythrolein, which are soluble in alcohol. Then by treating the residue with water a larger proportion of azolitmin is dissolved, and the solution is contaminated with very little of the other two principles.

Litmus test solution should be of such strength that 3 drops added to 50 mils of water will impart to the latter a distinct color. If one drop of $\frac{N}{10}$ acid or alkali solution be added to this the color should change to red or blue.

Litmus may be used in a very large number of titrations. It is of value in the titration of most mineral acids and of a few organic acids, e.g., benzoic and oxalic. It is also useful in the titration of alkaline hydroxids when the latter are free from carbonates.

But for carbonates, bicarbonates, etc., a reliable end-reaction can only be obtained by boiling the solution during the titration, in order to dispel the liberated CO_2.

Free CO_2 has an acid reaction with litmus, and interferes very much with the finding of the end-reaction.

Litmus may be used for ammonia and for borax. It is of no use for phosphoric or arsenic acid, nor for sulphurous acid, phosphates, or arsenates, because the change of tint is too gradual.

It is unsatisfactory in titrating many organic acids, e.g., tartaric and citric, but may be used for oxalic or benzoic, as before stated.

Sometimes it is required to perform a titration with litmus at night. Gas- or lamp-light is not adapted for showing the reaction satisfactorily, but by using a monochromatic light, such as the sodium flame, a very sharp line of demarcation may be found.

The operation should be conducted in a dark room, using

a piece of platinum foil sprinkled with salt or a piece of pumice-stone saturated with a solution of salt, heated in a Bunsen flame.

The red color then appears perfectly colorless, while the blue appears like a mixture of ink and water.

Luteol: alkalies = *Yellow*
acids = *Colorless*

Chemically it is an oxy-chlor-diphenyl-quinoxalin. It was suggested as an indicator by Autenrieth.

The solution for the purpose of an indicator is prepared by dissolving 1 part in 100 parts of alcohol. Of this, four drops are sufficient for 50 mils of fluid to be titrated.

In sensitiveness, luteol exceeds both litmus and phenolphthalein. It is more sensitive toward ammonia than Nessler's solution. Ten mils of a solution containing one drop of ammonia water per liter, is colored yellow immediately upon adding luteol, whereas with Nessler's solution it takes quite some time before a reaction is obtained.

Methyl Orange: alkalies = *Yellow*
acids = *Red*

Poirrier's Orange III, Tropæolin D, Helianthin, Mandarin-orange, Para-sulpho-benzeneazo-dimethylanilin.

This is prepared by the action of diazo-sulphanilic acid upon dimethylanilin; the acid so formed is converted into a sodium or ammonium salt, purified by reprecipitation with HCl, and again converted into a sodium or ammonium salt. If prepared carefully and from the purest materials, it is a bright orange-red powder, perfectly soluble in water and slightly in alcohol; but it is often found in commerce as a dull orange-brown powder, often not completely soluble in water. Many conflicting statements have been made by opera-

tors as to the value of methyl orange as an indicator, which have tended to bring this indicator into disrepute.

Sutton has examined many specimens, but has not found any in which the impurities sensibly affected its delicate action. He claims that the common error is the use of too much indicator, and that some eyes are more sensitive to a change of tint than others.

Methyl orange is no doubt a very good indicator, but practice with it must be had in order to obtain good results. The author has found one sample which had a beautiful orange color, but which was absolutely useless as an indicator.

A. H. Allen describes the characters and tests of a good article as follows:

1. Aqueous solution, not precipitated by alkalies. (Orange I becomes red-brown; orange II brownish-red.)

2. Hot concentrated aqueous solution yields with HCl microscopic acicular crystals of the free sulphonic acid, soon changing to small lustrous plates or prisms having a violet reflection. (Orange I gives yellow-brown color or flocculent precipitate; orange II brown-yellow precipitate.)

3. Dissolves in concentrated H_2SO_4 with a reddish or yellowish-brown color, which on dilution becomes fine red.

4. $BaCl_2$ yields a precipitate.

5. $CaCl_2$ yields no precipitate. (Orange I gives a red precipitate.)

6. $Pb(C_2H_3O_2)_2$ yields an orange-yellow precipitate.

7. $MgSO_4$ in dilute solutions precipitates the coloring matter in microscopic crystals.

Methyl-orange T.S. is made by dissolving 1 gm. of methyl orange in 1000 mils of water. Add to it carefully diluted sulphuric acid in drops until the liquid turns red and just ceases to be transparent. Then filter.

The great value of this indicator consists in the fact that

it is not affected by carbonic-acid gas, sulphureted hydrogen, or silicic, oleic, stearic and many other acids.

It answers well for ammonia, but it is useless for most of the organic acids. Phosphoric and arsenic acids are rendered neutral to methyl orange when only one third of the acid has combined with the base, the end-reaction being well defined. (Phenolphthalein indicates neutrality when two-thirds of acid are combined.)

This indicator should not be employed when titrating with standard solutions which are weaker than decinormal, nor should it be used in any hot titrations, nor in excessive quantities. Two drops are sufficient for 50 mils of the fluid to be titrated, or just enough to give it a faint tint.

Methyl Red: alkali = *Yellow*; acid = *Rose red*

(*Paradimethylaminoazobenzene - orthocarboxylic acid*) — $(CH_3)_2-N-C_6H_4-N=NC_6H_4\cdot COOH$. Violet crystals, very slightly soluble in cold water, yielding a red solution, readily soluble in alcohol and glacial acetic acid. When dissolved in sulphuric acid it shows the same color change as methyl orange. The applications of methyl red as indicator are the same as those of methyl orange, except in the case of titration of carbonates.

Methyl Red T.S. Dissolve 0.2 gm. of methyl red in 100 mils of alcohol. Its end-points are sharper than those of methyl orange, and it is far more sensitive for dilute solutions of weak bases, surpassing hematoxylin or iodeosin in the titration of alkaloids.

Phenacetolin: alkali { carbonates = *Red*; hydroxids = *Yellow* } acids = *Yellow*

This indicator is prepared by heating together for several hours equal molecular weights of phenol, glacial acetic acid, and sulphuric acid in a vessel provided with a reflux condenser. The product is then thoroughly washed with water to remove excess of acid and dried for use. It is only very slightly soluble in water, but dissolves readily in alcohol, forming a greenish-brown solution.

The solution yields with alkali hydroxids a scarcely perceptible pale yellow, but with normal carbonates of the alkalies, sulphids, and with ammonia it gives a decided pink color; with bicarbonates a more intense pink, while with acids a golden yellow.

This indicator is useful for estimating the amount of alkali or alkali earth hydroxids in the presence of carbonate, unless the hydroxid is present in too small a quantity. Ammonia must not be present. The titration is carried out by adding the acid until a faint red color appears; this indicates that the alkali hydroxid or the lime has been neutralized. The further addition of the acid intensifies the red until the carbonate present in the mixture is neutralized, when a golden-yellow color appears. The proportion of alkali hydroxid must be far in excess of the carbonate in order to obtain reliable results; furthermore, considerable practice is required in the use of this indicator in order to accustom the eye to the color changes.

A convenient strength of solution is 1 : 100 in alcohol.

Phenolphthalein ($C_{20}H_{14}O_4$): alkalies = *Red*, acids = *Colorless*

Preparation. Five parts of phthalic anhydrid ($C_8H_4O_3$), 10 parts of phenol (C_6H_6OH), and 4 parts of H_2SO_4 are heated together at 120° to 130° C. for several hours. The product is then boiled with water, and the residue, which consists of impure phenolphthalein, is dissolved in dilute soda solution and filtered. By neutralizing this solution the phenolphthalein is precipitated and may be purified by crystallization from alcohol; or the alcoholic solution may be boiled with animal charcoal, filtered, and the phenolphthalein reprecipitated by boiling water.

Uses. Phenolphthalein is a very valuable indicator; is extremely sensitive, and exhibits a well-marked and prompt change from colorless to pink, and *vice versa.* A few drops of the solution of the indicator show no color in neutral or acid liquids, but the faintest excess of alkali produces a sudden change to red.

It may be employed in the titration of mineral and organic acids and most alkalies, but it is not suited for the titration of ammonia or its salts. It is very sensitive to CO_2, and therefore in estimating carbonates the liquid must be boiled, as with litmus. It is inapplicable for borax, except in the presence of glycerin, because the color gradually fades away as the acid is added. One great advantage which phenolphthalein possesses is that its indications may be clearly read in many colored liquids; another is that it may be used in alcoholic liquids or in mixtures of alcohol and ether, and therefore many organic acids which are insoluble in water may be accurately titrated by its help.

Phenolphthalein T.S. is a one per cent solution in alcohol.

Poirrier Blue (C_4B): alkali { carbonates = *Blue*; hydroxids = *Red* } acids = *Blue*

This indicator, which is closely allied to Gentian Blue in properties, is obtained by the action of sulphuric acid on triphenylrosanilin. It is a blue powder with a coppery luster. It dissolves in water and in alcohol, yielding blue solutions. KOH and NaOH change the color to red, but ammonia decolorizes it. It is employed as an indicator in aqueous solution 1:500. This indicator is exceedingly sensitive to acids. Borax and boric acid give a blue color; in the titration of boric acid the red color does not appear until the acid is completely neutralized. This indicator is recommended for the titration of hydrocyanic acid, toward which it is especially sensitive, the alkaline cyanids are alkaline in reaction to most indicators, but C_4B does not show an alkaline reaction until the HCN is completely neutralized, and a minute excess of the alkali hydroxid has been added. C_4B is of the character of a weak acid and its salts are very unstable; they are decomposed by water alone when in very great dilution, therefore the indicator must be used in sufficient quantity. The addition of a few drops of alcohol facilitates the color change, which is indeed a very sharp one.

Resazurin: alkalies = *Blue*; acids = *Red*

This is a new indicator for alkalimetry, proposed by Crismer. It is prepared as follows: Dissolve 4 gms. of resorcin in 300 mils of anhydrous ether and add 40 to 45 drops of nitric acid (sp.gr. 1.25) saturated with nitrous anhydrid. Allow the mixture to stand in a cold place for two days, whereupon a deposit of blackish crystals, having a reddish-brown reflection, will be formed in the bottom of the vessel. The super-

natant clear red liquid is decanted and the crystals washed with ether until the washings show a blue color with ammonia water.

Resazurin ($C_{12}H_7NO_4$) is slightly soluble in water, more so in alcohol and freely soluble in acetic ether. It produces a blue solution with water, alkalies, and alkali carbonates, which are turned red upon the addition of a slight excess of acid. To use this indicator in alkalimetry, Crismer recommends the following solution: Resazurin 0.2 gm. dissolved in 40 mils of $\frac{N}{10}$ ammonia solution, and made up to 1000 mils with distilled water.

This is deep blue in color and keeps well. Two or three drops are sufficient to color 200 mils of liquid.

This indicator is not suited for the titration of nitric acid or monobasic organic acids, and it is not very sensitve to carbonic acid. It is, however, extremely sensitive to alkalies. If the solution is acidulated to a rose-red color and heated in a white glass flask, the solution will turn blue through the alkaline reaction of the dissolved glass before the boiling-point is reached.

This indicator is especially useful for borax.

Rosolic Acid ($C_{20}H_{14}O_3$): $\begin{matrix}\text{alkalies} = \textit{Red} \\ \text{acids} = \textit{Yellow}\end{matrix}$

This compound is also called Aurin and Coralline, and is prepared as follows:

A mixture of phenol and sulphuric acid is placed upon a water-bath, and oxalic gradually added, waiting each time till the evolution of gas ceases, and using less oxalic acid than is required to attack all the phenol.

In this process the oxalic acid is decomposed into CO,

CO_2, and H_2O. The CO immediately reacts with the phenol and forms rosolic acid, as the following equation shows:

$$3C_6H_5OH + 2CO = C_{20}H_{14}O_3 + 2H_2O.$$

Commercial rosolic acid is a mixture of several derivatives, among them the above, methylaurin $C_{20}H_{16}O_3$ and others. Commercial pœonin (also known as Aurin R.) [chiefly $C_{19}H_{14}O_3$] may be used in place of rosolic acid.

Rosolic acid is soluble in diluted alcohol. Its color is pale yellow, not changed by acid, but turns violet-red with alkalies.

It is an excellent indicator for the mineral acids and strong bases, weak ammoniacal solutions, oxalic acid and other organic acids, except acetic.

The test solution is made by dissolving 1 gm. of the commercial rosolic acid in 10 mils of diluted alcohol and then adding enough water to make 100 mils.

Tropæolin (OO): alkalies = *Yellow*; acids = *Yellowish-red*

This is used in the form of a solution containing 0.5 gm. to 1000 mils of alcohol.

Turmeric Tincture. Digest any convenient quantity of ground curcuma-root (from *Curcuma longa* Linné, nat. ord. *Scitamineæ*) repeatedly with small quantities of water, and throw this liquid away. Then digest the dried residue for several days with six times its weight of alcohol and filter.

Turmeric Paper. Impregnate white, unsized paper with the tincture and dry it.

The color principle of turmeric is curcumin. It is seldom used in volumetric analysis, except in the form of turmeric paper. For high-colored solutions curcumin gives no reaction

with acids, but becomes brown with alkalies. There is another color principle in turmeric besides curcumin, which is, however, useless in that it is indifferent to alkalies; it is soluble in water, and extracted by digestion with water, after which the curcumin is dissolved out with alcohol.

Turmeric paper is especially useful, because of its peculiar reaction with boric acid, with which it develops a brown color after drying, and which color, when touched with caustic soda solution is changed to dark green.

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